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INORGANIC CHEMISTRY.

LONDON : PRINTED BY
SPOTTISWOODE AND CO., NEW-STREET SQUARE
AND PARLIAMENT STREET

INTRODUCTION TO THE STUDY
OF
INORGANIC CHEMISTRY.



WILLIAM ALLEN MILLER, M.D.

D.C.L. LL.D.

*Late Treasurer and Vice-President of the Royal Society; Vice-President
of the Chemical Society; Professor of Chemistry in King's
College, London; Fellow of the University of London;
Honorary Fellow of King's College.*

NEW EDITION,

WITH QUESTIONS FOR EXAMINATION.

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1876

PREFACE.

THIS BOOK is written expressly for beginners. In order that they should really understand the statements which it contains, it will be necessary for them to begin at the beginning, and to go straight through it. Among other reasons for adopting this course, it is to be noted that it is impossible to avoid the use of technical terms in discussing a scientific subject; since we often have to deal with matters for which no expressions are in use in ordinary language. In this book, when a technical term is introduced for the first time, its meaning is explained, but the explanation is not afterwards repeated. Processes are also described in detail when first mentioned, but when afterwards referred to, they are simply directed to be followed.

Most of the experiments described are of a simple kind, and only require such apparatus and materials as may be easily constructed or procured. The student is strongly advised never to omit the performance of any experiment which he has the means of making. No useful knowledge of Chemistry can be acquired by any one unless he constantly makes experiments as he proceeds with the study.

W. A. MILLER.

NOTE.

MY FRIEND Professor MILLER completed this work, and placed the whole of the MSS., including the Preface, in the hands of the Printers. He was actually engaged in reading the proof sheets up to the time of his visit to the British Association Meeting at Liverpool, when he was seized with a sudden and fatal illness.

Professor Miller placed the first few sheets of the work in my hands, and requested me to read them and give him my opinion as to the mode of treatment. I accordingly did so, and suggested certain changes in the style and arrangement which, if adopted, might add to the clearness of the book and so far assist the young student in Chemistry. He approved of these suggestions, and in his last illness left a written request that I would see the work through the press. I have to the best of my ability complied with his wishes.

C. TOMLINSON.

HIGHGATE, N.

November 10, 1876.

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INORGANIC CHEMISTRY.

CHAPTER I.

CHEMICAL ELEMENTS—COMBINATION.

(1) *Scope and aim of Chemistry.*—Many of the changes in natural objects which are taking place around us every day—some slowly, some quickly—are the result of a class of actions which are called *chemical*. When, for instance, a piece of iron is exposed to the open air and becomes covered with rust, or when a fallen leaf crumbles away, or when milk becomes sour after it has been kept for a few days, the change which has occurred in each case is of a chemical nature; in all of them an alteration in the composition of the substance has taken place, and new substances, with properties quite different from those of the original material, have been formed. The iron has taken up something from the air which has altered its colour and lessened its strength; the leaf has furnished new bodies, some of which have passed off unseen into the atmosphere; while the sugar in the milk has become changed into an acid, and the curd has been separated from the whey.

It is the business of the chemist to find out what these various substances are made of, as well as the exact nature of the alteration in composition which has occurred in these cases, and the means by which such changes can be

forwarded or varied, or altogether prevented. Chemistry is in fact the science which teaches us the composition of bodies. Whenever, therefore, a new substance is put into the hands of the chemist, whether it be derived from the mineral, the vegetable, or the animal creation, one of his first questions is, Of what is this body made? Is it composed of one kind of matter or of several kinds?

In order to obtain answers to these questions we must learn to observe carefully the changes which are going on around us; and we must also contrive fresh arrangements, more or less altered, in which the exact circumstances have been planned by ourselves for the purpose of seeing what will happen under these altered conditions. Such planned observations are what are commonly called *experiments*; and the better they are planned and performed the more we shall be able to learn if we reason accurately upon the result obtained. Chemistry is in the best sense an experimental science, calling into action alternately the head to plan, the hands to perform, and the head again to explain the results of our experiments.

Various substances may easily be shown to contain more than one kind of matter; while others have hitherto foiled all the efforts made to separate from them any second substance. For example, from a mass of pure silver nothing can be obtained but silver itself, copper will furnish nothing but copper, and from sulphur the chemist can extract nothing but sulphur. Such bodies have therefore been called *undecomposed* or *simple substances*, or *chemical elements*.

On the other hand, such bodies as table salt, iron rust, water, chalk, wood, mercuric oxide, may each by the use of suitable means be made to yield more than one kind of matter.

Experiment 1.—Place a scrap of wood in a test-tube, which is a glass tube about the size of the forefinger, and closed at one end. Heat it by holding it just above the flame of a spirit lamp. The wood will become charred and blackened while

Vapours will be given off, and will collect on the cold sides of the glass in the form of a brownish tarry liquid.

Exp. 2.—Place in a test-tube as much mercuric oxide, or red oxide of mercury, as will cover a sixpence, and heat the end of the tube in the flame of a spirit lamp. Oxygen gas will come off as a colourless gas, in which a splinter of wood, previously kindled and introduced into the tube, will burn brilliantly, and drops of metallic mercury will collect on the cold sides of the tube.

Such bodies as wood and mercuric oxide are said to admit of being *decomposed*, that is, they may be separated into two or more distinct kinds of material; and all substances which thus admit of being *analysed* or pulled asunder into their constituent substances are known chemically as *compounds*.

In many cases the chemist can not only separate a compound into its elements, but he can, out of those elements, by *synthesis*, or putting them together again, build up the compound—as may easily be done with the iron rust, and the mercuric oxide just mentioned. When a body can be thus separated into its elements, and can be reproduced by combining those elements again with each other, we possess the most complete proof of its chemical composition, though much remains to be discovered respecting the mode in which the different substances are arranged in the compound. We may know, for example, what letters are wanted to spell a particular word, but in order to spell the word correctly we must also know the order in which these letters are to follow one another. Just so it is necessary to discover if possible the arrangement of the elements in a chemical compound before we can be said truly to know its constitution. Every material object with which we are acquainted is, in a chemical point of view, either an element or a compound, or else a mechanical mixture of two or more elements or compounds.

By far the greater number of natural objects are com-

pounds. These compounds consist of two or more simple substances united according to certain fixed rules or laws. The simple bodies have no more likeness to the compounds which they form than the separate letters of the alphabet have to the words which may be made from them. The power which causes the various elements to unite one with another, and which holds them together after they have united, is called *chemical attraction*. It is much stronger between some elements than others, and is exerted according to special rules, which will be explained hereafter.

(a) *Chemical Elements : their mode of occurrence.*—Two of the most important of the elements, oxygen and nitrogen, form the principal portion of the atmosphere, and they occur in it mixed with each other, but not chemically combined. The only other elements of importance which are met with in their separate or *native* state are sulphur or brimstone, carbon (in the very different forms of black-lead and diamond), iron, copper, bismuth, mercury, silver, gold, and platinum; but some of these are found much more abundantly in combination with other elements than in the separate form.

The chemical elements are little more than sixty in number. Most of them occur in combination in the strata of the earth. Some, indeed, are found so sparingly that their properties have been but little examined. Others again are extremely abundant, particularly hydrogen, oxygen, nitrogen, and carbon; two or more of these four elements enter into the formation of most of the objects familiar to us, except the ordinary metals, which are themselves elementary bodies.

Taking the earth as a whole, so far as man has been able to penetrate into and examine it, more than one-third of it has been found to consist of oxygen either combined or uncombined, and nearly one-fourth consists of silica in combination, for the most part, with oxygen. Besides this, compounds of aluminum, calcium, iron, carbon, magnesium,

sodium, potassium, and sulphur, are found in considerable proportion; some confined to special places, and the others very generally diffused: while, dissolved in sea water, we have, independently of the oxygen and hydrogen of the water, compounds of sodium, chlorine, magnesium, calcium, and potassium, in addition to combinations of about twenty other elements in extremely small proportions.

For the sake of convenience the elements are divided into the two classes of *metals* and *non-metals*, though the two classes run into each other. Fifty of the elements are commonly reckoned as metallic, and thirteen as non-metallic in their nature. The thirteen elements commonly enumerated as non-metals are oxygen, nitrogen, hydrogen, carbon, chlorine, bromine, iodine, fluorine, sulphur, selenium, phosphorus, silicon, and boron.

In the following list those of the greatest importance are printed in capitals, as OXYGEN. The chemical properties of these we shall examine hereafter; those in ordinary type, as Bromine, will be touched upon less fully; whilst of those in italics, such as *Tantalum*, owing to their rarity, and the absence of any important application of them in the arts, few will need more than a passing mention.

ELEMENTS WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

Name	Symbol	Atomic Weight	Name	Symbol	Atomic Weight
ALUMINUM	Al	27.5	Cerium	Ce	92.1
Antimony (<i>Stibium</i>)	Sb	122	CHLORINE	Cl	35.5
Arsenicum	As	75	Chromium	Cr	52.5
BARIUM	Ba	137	Cobalt	Co	59
Bismuth	Bi	210	COPPER (<i>Cuprum</i>)	Cu	63.5
Boron	B	11	<i>Didymium</i>	D	96
Bromine	Br	80	<i>Erbium</i>	E	112
<i>Cadmium</i>	Cd	112	Fluorine	F	19
<i>Cesium</i>	Cs	133	<i>Gadolinium</i>	G	95
CALCIUM	Ca	40	Gold (<i>Aurum</i>)	Au	197
CARBON	C	12	HYDROGEN	H	1

ELEMENTS WITH THEIR SYMBOLS AND ATOMIC WEIGHTS—*cont.*

Name	Symbol	Atomic Weight	Name	Symbol	Atomic Weight
<i>Indium</i>	In	76	<i>Rhodium</i>	Ro	104
Iodine	I	127	<i>Rubidium</i>	Rb	85
<i>Iridium</i>	Ir	197	<i>Ruthenium</i>	Ru	104
IRON (Ferrum)	Fe	56	<i>Selenium</i>	Se	79.5
<i>Lanthanum</i>	La	92	SILICON	Si	28
LEAD (Plumbum)	Pb	207	SILVER (Argentum)	Ag	108
<i>Lithium</i>	L	7	SODIUM (Natrium)	Na	23
MAGNESIUM	Mg	24	<i>Strontium</i>	St	87.5
MANGANESE	Mn	55	SULPHUR	S	32
MERCURY (Hydrargyrum)	Hg	200	<i>Tantalum</i>	Ta	182
<i>Molybdenum</i>	Mo	96	<i>Tellurium</i>	Te	129
Nickel	Ni	59	<i>Thallium</i>	Tl	204
<i>Niobium</i>	Nb	94	<i>Thorium</i>	Th	232
NITROGEN	N	14	Tin (Stannum)	Sn	118
<i>Osmium</i>	Os	199	<i>Titanium</i>	Ti	50
OXYGEN	O	16	Tungsten (Wolframium)	W	184
<i>Palladium</i>	Pd	106	<i>Uranium</i>	U	120
PHOSPHORUS	P	31	<i>Vanadium</i>	V	51
Platinum	Pt	197	<i>Yttrium</i>	Y	62
POTASSIUM (Kalium)	K	39	ZINC	Zn	65
			<i>Zirconium</i>	Zr	89

(3) *Chemical Notation* -- In the foregoing table it will be seen that opposite to the name of each element is placed its *chemical symbol*, which consists of the first letter of its Latin name. Where two or more of these names begin with the same letter, a second letter is added to distinguish such symbols from each other. These symbols form a simple and easy kind of shorthand, by means of which chemical changes may be clearly and compactly represented.

It is important to remark that whenever the symbol of any element is used, it represents not merely the element itself, but a definite quantity of that element. For instance, the symbol O always stands for 16 parts by weight of oxygen, the symbol H always stands for 1 part by weight of hydrogen, and in the table opposite to the symbol of

* Each element is placed the number of parts[†] of the element which that symbol represents. To render our ideas precise, we will suppose that H stands for 1 gram of hydrogen; then O will represent, not 1 gram, but 16 grams of oxygen; C will represent 12 grams of carbon; S 32 grams of sulphur, and so on. The reason why these particular numbers are appropriated in the table to their corresponding elements will be explained hereafter. They constitute a very important series of constants, which, in the case of the more important elements, it will be found highly useful to commit to memory. These numbers represent what chemists have termed the *atomic weights* of the elements. Every element is supposed to be made up of excessively small particles or atoms exactly of the same size and weight in the same body. If the atom of hydrogen be supposed to weigh 1, the number opposite to each element in the table represents the weight of its atom, or smallest particle, compared with that of the atom of hydrogen.

Compound bodies may also be represented by symbols; and the proportion as well as the nature of the elements concerned is easily expressed by writing the symbols side by side: HCl, for instance, represents hydrochloric acid, a compound of hydrogen with chlorine, in which the proportion of 1 gram of hydrogen is united with 35.5 grams of chlorine; H₂O indicates water, a compound of hydrogen with oxygen, the figure 2 below the symbol H multiplies the quantity of hydrogen by 2, and represents 2 grams of hydrogen combined with 16 grams of oxygen. When two or more chemical symbols are thus written side by side, they constitute a *chemical formula*. Whenever the sign + is placed between two formulæ, it is employed to show that the two bodies have been mixed with each other. The

* Another unit of weight might have been taken, such, for instance, as 1 grain, or 1 ounce, or 1 pound; then O would stand for 16 grains of oxygen, 16 ounces of oxygen, or 16 pounds of oxygen, according as a grain, an ounce, or a pound of hydrogen was the unit chosen for the comparison.

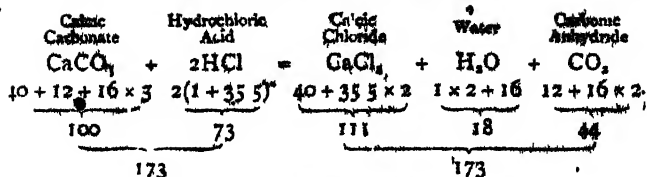
sign $=$ does not indicate identity or absolute equality, but is usually employed in the sense of the word 'yields;' and when it connects the two halves of a chemical equation, it represents that if the compounds which stand before it are mixed with each other, with due precaution, a chemical change will occur which may be represented by the arrangement of the symbols placed after the sign $=$. For instance, in the chemical equation,



CaCO_3 is the chemical formula for calcic carbonate, of which marble is one of the many forms; and if H represents 1 gram of hydrogen, CaCO_3 will represent 100 grams of marble, since Ca stands for 40 grams of calcium, C for 12 grams of carbon, O₃ for 3 times 16 or 48 grams of oxygen, making together 100 grams. HCl is the chemical symbol for hydrochloric acid; and since H means 1 gram of hydrogen, Cl 35.5 grams of chlorine, 2HCl will mean twice that quantity, or 73 grams of hydrochloric acid. As soon as the hydrochloric acid is poured on the marble, a chemical change occurs; the marble is dissolved, and an effervescence* is produced, the result being the production of calcic chloride, CaCl_2 , containing 40 grams of calcium, twice 35.5 or 71 grams of chlorine, making together 111 grams of calcic chloride; H_2O , 18 grams of water, containing 2 grams of hydrogen, and 16 grams of oxygen; while CO_2 stands for 44 grams of carbonic anhydride (or carbonic acid), containing 12 grams of carbon with twice 16 or 32 grams of oxygen, and this has passed off as a gas, and produced the effervescence.

The whole may be represented as follows, where the figures written under each symbol represent the number of grams of each element or combination of elements:—

* A body is said to *effervesce* when it gives off gas suddenly with an appearance of boiling.



Or in words: Mix 100 grams of marble with a solution of 73 grams of hydrochloric acid: it will yield 111 grams of calcic chloride, 18 grams of water, and 44 of carbonic anhydride.

Whenever a chemical compound is formed, the same compound is always found to contain the same elements, united in fixed and invariable proportions; 100 parts of marble *always* contain 40 of calcium, 12 of carbon, and 48 of oxygen: and in like manner 18 parts, whether grams, pounds, or tons of water, always contain 2 parts of hydrogen and 16 parts of oxygen, be they grams, pounds, or tons.

(4) *Weights and Measures.*—The weights and measures used in this work are those of the metric system, which, on account of their simplicity and convenience, are now commonly employed by men of science throughout the world. This uniformity of usage does away with the waste of time formerly incurred in converting the weights and measures of one country into those of their neighbours. As, however, most persons in this kingdom have been accustomed from infancy to a different system in the transactions of daily life, it will be necessary to explain the principles of the metrical system. It will be needful to bear in mind that the *metre* or *unit of length* is equal to 39.37 English inches; and consequently that 10 centimetres represent very nearly 4 inches, while a millimetre is almost exactly $\frac{1}{25}$ th of an inch. The subdivisions of the metre are marked by the Latin prefixes *deci*, ten, *centi*, a hundred, and *milli*, a thousand; so that the tenth of a metre is called a *decimetre*, the hundredth of a metre a *centimetre*, and the thousandth of a metre a *millimetre*. The higher multiples are indicated by the Greek prefixes *deca*, ten, *hecto*, one

hundred, *kilo*, one thousand; but the prefix *kilo*, or multiple by one thousand, is almost the only one used in practice. For instance, the higher multiple, or 1000 metres, is called a *kilometre*. It is used as a measure of distance by road, and represents about 1094 yards, 16 kilometres being equal to nearly 10 English miles.*

Fig. 1.

Each side of this square measures

1 Decimetre, or
10 Centimetres, or
100 Millimetres, or
3.937 English inches.

A *litre* is a cubic measure of 1 decimetre in the side, or a cube each side of which has the dimensions of this figure.

When full of water at 4° C. a litre weighs exactly 1 *kilogram* or 1000 grams, and is equivalent to 1000 cubic centimetres; or to 61.024 cubic inches, English.

A *gram* is the weight of a centimetre cube of distilled water; at 4° C. it weighs 15.432 grains.

1 sq.
Centim.

4 inches.

* The metre is a bar of platinum deposited in the archives of France, and when made it was believed to represent exactly the ten-millionth part of a quadrant of a great circle encompassing the globe of the earth on

The *measures of capacity* are connected with those of length by making the unit of capacity in this series a cube of one decimetre, or 3.937 English inches, in the side; this, which is termed a *litre*, is equal to 1.7637 imperial pints, or to 61.024 cubic inches.

Finally, the *system of weights* is connected with both the preceding systems by taking as its unit the weight of a cubic centimetre of distilled water at 4° C.: it weighs 15.432 English grains. The *gram*, as this quantity is called, is further subdivided into tenths or *decigrams*, hundredths or *centigrams*, and thousandths or *milligrams*, the milligram being equal to about $\frac{1}{28}$ of a grain.

The higher multiple of 1000 grams constitutes the *kilogram*. It is the commercial unit of weight, and represents 15,432 English grains, or rather less than 2½ lb. avoirdupois.

The weight of 1000 kilograms, or a cubic metre, of water, is 0.9842 of a ton, which is sufficiently near to a ton weight to allow of its being reckoned as one ton in rough calculations.

The temperatures given in this book are expressed throughout in degrees of the centigrade thermometer, unless otherwise specified. The following is a short comparative table of the two scales, Centigrade and Fahrenheit.

C	F	C	F	C	F	C	F
-20	-4°	15	59°	45	113°	75	167°
-15	+5	20	68	50	122	80	176
-10	14	25	77	55	131	85	185
-5	23	30	86	60	140	90	194
0	32	35	95	65	149	95	203
5	41	40	104	70	158	100	212
10	50						

the meridian of Paris. But it has been found by later and more accurate measurements that this assumption is erroneous. The metric system is, however, no way dependent upon the accuracy of this assumption, and the actual bar of platinum then made continues notwithstanding to be the unit of the metric system.

(5) *Physical States of Matter.*—Most of the simple bodies of the chemist occur as solids at the common temperature of the air; two only, mercury and bromine, exist as liquids; while four others, viz. oxygen, hydrogen, nitrogen, and chlorine, are known as gases; but in one or other of these three forms of *solid*, *liquid*, or *gaseous* every substance exists, whether it be simple or compound.

Solid bodies, such as a bar of iron or a block of wood, have a definite form, which cannot be altered without the application of some force more or less considerable.

Liquids, on the contrary, like water, when placed in an open vessel yield to the slightest force: their particles slide easily over each other; they adapt themselves at once to any unevenness of the bottom or sides of the vessel, and they always present a level surface in an open vessel. They do not become smaller by compression in closed vessels to any extent which can be seen by common observation.

Gases, on the other hand, like air, yield easily to compression. In closed vessels, when the pressure upon them is increased, it can be seen that they are forced into a smaller space; and when the pressure is lessened the space filled by the gas becomes larger. Hence gases are sometimes spoken of as *elastic fluids*. They are always tending to increase in bulk, and they always completely fill the vessel which contains them, no matter how irregular may be its shape.

Many bodies may be made to assume either of these three states at pleasure, and to pass slowly backwards and forwards from one condition to the other for any number of times by simply altering the degree of heat to which they are exposed. Ice, water, and steam, for example, are the same chemical substance in three different physical states, and the same quantity of water may be raised into steam, and converted back again into water or into ice as often as may be desired. The alteration of the form of a body does not affect its weight. A gram of ice when changed into steam still weighs a gram although we no longer see it; and

every litre or other fixed measure of each has a definite weight, as may be easily proved by the use of proper means.

All the solid elementary bodies except carbon have been melted, though some require a very intense temperature. Some of the metals, such as platinum and a few of the metals which accompany it in its ores, cannot be melted in ordinary furnaces; but the extreme heat of the voltaic arc or the electric current produced between the poles of the voltaic battery converts all the metals not merely into liquids but even into vapour, and at this exceedingly intense heat all compounds are separated into their elements. On the other hand, most gases may, by the united action of cold and great pressure, be reduced to the liquid state; among these are chlorine, sulphurous anhydride, carbonic anhydride, and hydrochloric acid; several of these have also been frozen by intense cold into masses like ice or snow. A few gases, including the elements oxygen, hydrogen, and nitrogen, have never been liquefied, though it can scarcely be doubted that their liquefaction, and even freezing, would be effected could we apply a still more intense degree of cold and pressure combined.

(6) *Mixture distinguished from Combination.*—When once a chemical compound has been formed its components cannot, as a rule, be separated by merely mechanical methods. A piece of marble, as we have seen (p. 8), consists of three elementary bodies—carbon, oxygen, and calcium. It is easy to grind the marble to a powder of extreme fineness, but every fragment of that powder is still marble, and no one by mere grinding could separate the carbon, the oxygen, and the calcium from each other. The *molecule* or minutest particle of marble which can exist separately is still a compound substance formed of still smaller particles or *atoms*, of the elements carbon, oxygen, and calcium. To accomplish the separation of these atoms, which together form the molecule of marble, we must employ some new power; and one which the chemist finds his most useful ally in such cases is

heat. If the marble be heated for a time to bright redness it is decomposed. The carbon with part of the oxygen is driven off as a compound gas, and the calcium with the rest of the oxygen remains behind in the form of the solid compound, lime. Still, by this means a partial separation only of the three elements has been effected, two new compounds having been formed instead of the original one.

Again, it seldom happens that by mechanical means alone we can make two bodies unite chemically with each other. In making gunpowder, for example, which is a mixture of sulphur, charcoal, and nitre, the three substances are first ground separately to a fine powder. They are then mingled together, moistened with water, and ground for several hours under edge stones, in order to mix them as intimately as possible: after this they are subjected to intense pressure, and finally broken up into grains. But, notwithstanding all this, gunpowder still remains only a mechanical mixture of its three components, nitre, charcoal, and sulphur. The nitre may be washed out of the mixture by means of water; the sulphur may be dissolved out of the remainder by means of carbon disulphide, and the charcoal will be left. On evaporating the water the nitre may be recovered unaltered; and on allowing the disulphide to volatilise or escape in vapour, the sulphur will remain behind. But the mixed materials are ready in gunpowder to act chemically upon each other; for if a spark fall upon the powder a sudden change occurs, a flash follows, and a prompt chemical action takes place, in consequence of which a large volume of gas is produced, while the heap of powder is converted into new substances, several of which are gases, and none have any resemblance to the original materials.

Mechanical *mixture*, then, and chemical *combination* are two very different things; they ought never to be confounded with each other, although the mistake is often made by beginners. Whilst in every true chemical compound the proportion of its constituents is perfectly fixed, in a

mechanical mixture the proportions of the substances of which it is made may be altered to any extent that may be desired; besides this, the mixture always preserves properties which are intermediate between those of its components. A mixture of table salt and sugar, for instance, may be made by grinding the two together, and the quantity of either may be varied at pleasure. Its flavour will partake of the saline taste of the one, and of the sweetness of the other; the degree of saltiness will vary according as the proportion of salt to the sugar is increased or diminished. But each particle of salt and of sugar, however small, still continues a true chemical compound unaffected by the other, and in each of them the quantity of the constituent elements is unchanged.

Further, in the case of every true chemical compound, not only are the proportions of its constituent elements fixed, but the properties of the compound, for the most part, differ totally from those of the separate elements which form it, as well as from those of the mixture of the two elements before they have become chemically united. The truth of this we shall see as we proceed, and the first case in which we shall have occasion to observe it is in the chemical properties of the air, which we shall now examine.

CHAPTER II.

A. THE NON-METALS.

ATMOSPHERIC AIR. OXYGEN—NITROGEN.

(7) *The Atmosphere not an Element.*—We are surrounded on all sides by a viewless substance, the air, which though commonly unnoticed, makes itself felt at once in every gust of wind which blows. Every 'empty' vessel, as it is usually called, is really full of air.

Exp. 3.—Take a glass bottle and press it with its mouth downwards into a basin of water. The water will not fill the bottle, for it is already full of air. Now turn the mouth of the bottle upwards, still keeping it under water; bubbles of air will escape, and when all the air has thus been allowed to pass out the bottle will have become full of water.

So lately as a hundred years ago the air was thought to be an element; but it may easily be shown that it is truly a mixture of several different substances, some of which are simple bodies, and others are chemical compounds.

Fig. 2.



Exp. 4.—Fasten a short bit of candle to a flat piece of cork (Fig. 2). Float it on some water in a soup plate; light the candle, and place a jar full of air with its mouth downwards over it. In a few minutes the candle will burn dimly, and then will go out.

The air which is left will no longer allow a candle to burn in it; it has become altered in its properties by the burning of the candle, and has experienced an important chemical change. Other substances besides a burning candle will produce chemical changes in the air.

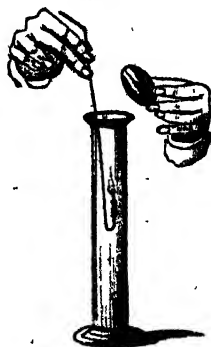
Exp. 5.—Take a glass jar 6 or 8 centim. in diameter and 25 cm. high; moisten it upon the inside, and sprinkle over the moistened surface a thick layer of iron filings; then place it, with its open end downwards, over water in a soup plate, and set it aside in a warm room for a day or two: the iron filings will gradually grow rusty, the bulk of the air in the jar will become less, and the water will rise slowly until it stands about 5 centim. higher in the jar than it did at first; after this the bulk of the enclosed air will not be further lessened. If a flat plate of glass be now slipped under the open end of the jar, the whole may be lifted out of the water; and on placing it mouth upwards, and then removing the glass plate, and at once putting into the jar a lighted taper fastened to a wire, as shown in Fig. 3, the taper will immediately cease to burn.

The iron in rusting has taken away something from the air which enabled the taper to burn in it; and that something is the elementary gas called oxygen.* The remainder of the air in which the taper will not burn consists chiefly of another gaseous element, called nitrogen.

The candle in burning, Exp. 4, also took oxygen from the air, and it went out as soon as it had taken up a certain quantity of the oxygen contained in the air enclosed by the jar.

Other metals besides iron may be used to remove oxygen from the air, particularly if they are heated with it. If mercury be used for the purpose, it will not only remove the oxygen, but it may be afterwards made to give it up again in a separate form.

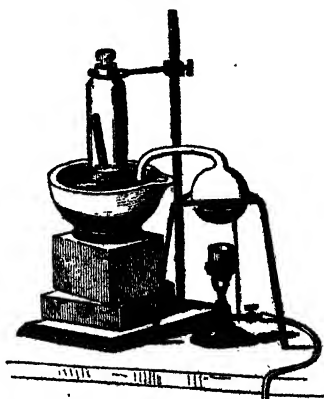
Fig. 3.



Exp. 6.—This experiment requires some days to complete it, but it is very instructive, and may be made in the following manner :—

Into a dry flask provided with a neck 50 centim. or more in length introduce about 40 grams of clean mercury; then bend the neck of the flask twice upon itself, into the form shown in Fig. 4, and plunge the bend into a small Wedgwood-ware mortar, containing mercury, so as to leave the open end of the neck projecting above the surface of the metal into a jar containing

Fig. 4.



air, which is to be supported over it. Now apply the heat of a lamp to the flask, and keep the mercury for two or three days at a point just below that necessary to make it boil. Red scales will be formed slowly upon the surface of the mercury in the flask; and these scales after a time will no longer increase in quantity. If the lamp be then withdrawn, and the whole allowed to cool, the bulk of the air will be found to have become considerably less. The hot mercury has acted chemically on the air both of the flask and of the jar, owing to the free passage of both portions through the neck.

The gas which is left consists almost entirely of nitrogen. On adding mercury till the height outside and inside the jar is the same, and then withdrawing the stopper and introducing a lighted taper, supported on a wire handle, it will be put out. A mouse or other small animal would also soon die if plunged into it. The oxygen is the portion of the air necessary to support the life of animals. If one or two grams of the red scales formed by thus heating mercury in air be placed in a test tube, they may be made to give up the oxygen again by heating them still more strongly.

Exp. 7.—Fit a good cork to the mouth of the tube; then withdraw the cork, and with a round file bore a hole through it, just

Fig. 5.



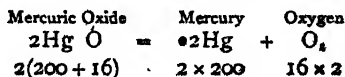
large enough to admit a narrow glass tube, bent as shown in Fig. 5. Heat the tube and the red scales in the flame of a spirit lamp while the

open end of the narrow tube is dipped under water. Bubbles of gas will soon begin to come off. Next fill two or three narrow jars or wide test tubes with water; close them with the finger, and invert them in the basin; collect the bubbles of gas in one of them as they escape from the narrow tube. The first jar will be filled chiefly with the air originally in the heated tube; this may be thrown away; but if into one of the other tubes, when filled with

the gas, a splinter of wood on the end of which is a glowing spark be plunged, the wood will burst into a flame.

The mercury used in the flask, Fig. 4, has in fact separated the atmospheric air into two portions, one of which, the nitrogen, will not allow a candle to burn in it, and is left unacted upon by the metal; while the portion which is active in supporting flame has combined with the mercury, and converted it into the red scales. When these scales are heated more strongly, they become separated into metallic mercury, and into the gas which, as we have seen, is highly fitted both for the support of life and for the burning of such bodies as may be kindled in the open air. This gas is called *oxygen* (the 'acid producer'), because it forms a needful part of many acid bodies.

A fixed weight of mercury will always unite with a fixed quantity of oxygen. For instance, 400 grams of mercury will combine with exactly 32 grams of oxygen, and will form 432 grams of the red oxide. If, again, 432 grams of these red scales of mercuric oxide be decomposed by heat, and proper care be taken to collect the whole of what is given off, 400 grams of liquid metallic mercury would be found, and 32 grams, or about 22·4 litres, of gaseous oxygen. These changes may be represented in symbols as follows; the quantities of each substance are written beneath:—



(8) OXYGEN: *Symbol*, O; *Atomic Weight*, 16; *Atomic Volume*, \square ; *Specific Gravity*, 1·10563; *Relative Weight*, 16;* *Molecular Weight*, O_2 , 32; *Molecular Volume*, \square .†

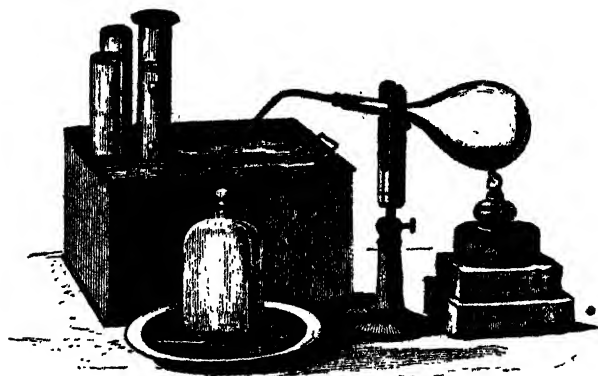
Exp. 8.—There are other means of obtaining oxygen: one of the best is by heating potassic chlorate (KClO_3). This salt may

* See page 30.

† See the chapter on the Atomic Theory for an explanation of these terms.

be mixed with about its own weight of black manganese oxide in fine powder. This oxide should be first made red hot in a covered clay crucible, and allowed to cool; it should then be ground up in a clean mortar with the chlorate. The manganese oxide enables the oxygen to pass off from the chlorate at a much lower heat than is needed if the salt is heated alone, although the oxide itself undergoes no permanent change. 30 or 40 grams of this mixture may be put into a clean and dry Florence oil flask, provided with a good cork, through which is passed a tolerably wide bent glass tube. The flask is to be placed with the end of the tube dipping under the water in the *pneumatic trough*, Fig. 6. If the mixture in the flask is heated over a lamp, gas comes off freely, and may be collected in jars placed for its reception.

Fig. 6.



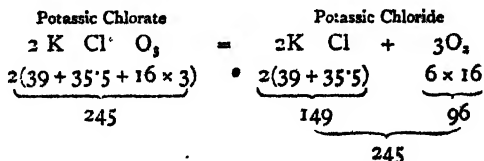
A pneumatic trough for experiments upon gases may be easily made out of a small tub or pan, which is to be nearly filled with water. A shelf must be fixed at one end, so as to be 3 or 4 centim. below the surface of the water, or the glass jar may even be supported on a brick; 3 or 4 jars, each holding about a litre, may be used to receive the gas. They should be open below, and one or two may be provided with a glass stopper ground to fit the neck. They

may be filled with water in the trough, and placed with the bottom downwards on the shelf. As they become filled one after another with the gas, they can be removed by sliding a plate under each, while the mouth is still under water, and then lifting the plate and jar together out of the trough.

Though the potassic chlorate is more easily decomposed when mixed with manganese oxide than when heated alone, the pure salt may be made to give off oxygen by heating it more strongly by itself.

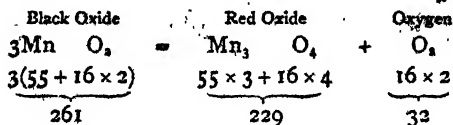
Exp. 9.—Place about a gram of the salt in a test tube, and heat it over a spirit lamp. The chlorate snaps and flies to pieces, or *decrepitates*, when first heated. It then melts and forms a clear liquid, which, when heated more strongly, gives off bubbles of pure oxygen gas. The mass gradually becomes white and opaque, and ceases to give off oxygen, leaving a white residue, consisting of chlorine and potassium only, and known as potassic chloride. The gas at first often looks cloudy, owing to little particles of the salt which are carried over suspended in it in fine powder, but these gradually become dissolved in the water.

245 grams of the chlorate would give off 96 grams of oxygen, or about 67.2 litres of the gas. The change may be thus represented:—



If the mineral known as black manganese oxide (MnO_2) be made red hot, oxygen may also be obtained from it; but only one-third of its oxygen is thus driven off, or about one-ninth of the weight of the mineral if pure. The ore of manganese, however, always contains impurities, which cause the oxygen gas to be mixed with more or less of other gases. The black oxide when heated becomes converted, with loss

of oxygen, into a reddish-brown oxide of manganese: 261. grams of pure black oxide would yield 32 grams of oxygen. or 22.4 litres of gas.



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Exp. 10.—Procure a gaspipe or an iron tube 3 or 4 centim. in diameter, 40 or 50 cm. long, closed at one end, and provided at the other with a cork, through which is passed a long piece of pewter or copper tubing; place 50 or 100 grāms of the oxide in small lumps in the tube, and make the closed end of the iron tube red hot: gas will be driven off, and may be collected over water.

Red lead, nitre, and several other substances, also give off oxygen, more or less pure, when heated; but either potassic chlorate, or manganese oxide, or the mixture of both, is the substance from which it is usually and most easily obtained.

Oxygen is a clear, transparent, colourless gas, which has never been liquefied by cold or pressure; it has no smell or taste. No other gas can be used instead of oxygen for the support of respiration in man and animals; but it cannot be safely breathed in a pure state for any length of time, as it would over-excite the bodily frame. The nitrogen, with which it is mixed in the air is needed to dilute it, so that it may be respired with safety. Oxygen is attracted by a magnet like iron.

Oxygen is remarkable for its great chemical activity. It will combine with each of the elementary bodies, with the single exception of fluorine. Substances which will burn in air burn in oxygen with much greater energy, as may be further shown by the following experiments:—

Exp. 11.—Fasten a piece of baky charcoal to a stout wire; pass the wire through a small flat board or a piece of tinplate. Kindle the charcoal by holding it in a flame; then hang it in a

jar of oxygen. It will burn away rapidly, with a steady glow, throwing out sparks, or *scintillations*, and will produce a new colourless gas, called carbonic anhydride, or carbonic acid (CO_2).

Exp. 12.—Place a little sulphur in a small copper spoon on the end of a wire, called a deflagrating spoon; heat it in the flame of a spirit lamp till it takes fire, and suspend it in like manner in another jar of oxygen. The sulphur will burn with a lilac flame, and on uniting with the gas will form an invisible substance with a pungent odour, called sulphurous anhydride (SO_2).

Exp. 13.—Cut off a piece of phosphorus of about the size of a pea from a stick of phosphorus under water.* Dry it carefully on a bit of blotting-paper, and put it into a copper spoon, also suspended from a wire. Touch it with a hot wire: it will take fire. Plunge it at once into oxygen: it will burn with dazzling brilliancy, and form white fumes of phosphoric anhydride (P_2O_5).

Many substances which will scarcely burn in air *deflagrate*, or burn with violence, in oxygen:—

Exp. 14.—Heat a piece of watch-spring red hot for a few moments in the fire; let it cool, and then twist it into a spiral. Heat one end slightly, and dip it into a little powdered sulphur, and pass the other end through a cork. Set fire to the sulphur, and immediately plunge it into a jar of oxygen, supporting it in the neck of the jar by the cork. The burning sulphur will set fire to the steel, which will burn with great splendour, while drops of melted oxide of iron (Fe_3O_4) will run down and fall upon the plate below.

Exp. 15.—Zinc foil cut into the form of a tassel, if it be tipped with sulphur to enable it to take fire, may be kindled and will burn in oxygen with a dazzling white light, forming zinc oxide (ZnO).

Exp. 16.—Place a piece of potassium † of the size of a pea in

* Phosphorus is extremely inflammable; it must always be kept under water, and should not be handled with the warm hand except under water.

† Potassium is the metal contained in pearl-ash; it must always be kept under naphtha, and must not be touched with the fingers, or with anything that is wet.

a copper spoon, heat it in the flame of a spirit lamp till it begins to glow; then introduce it into a jar of oxygen. It will burn, and a quantity of white solid potash (K_2O) will be formed in the spoon by the union of oxygen with the potassium.

The compounds which oxygen forms with other elements are called *oxides*, and the act of combination of any substance with oxygen is called *oxidation*. The experiments above described are instances of this process, and in each case a compound is produced entirely different in properties both from the oxygen and from the body burned.

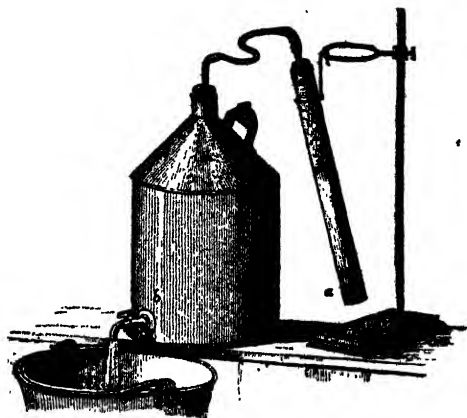
(9) *Combustion*.—Whenever any rapid chemical action takes place, attended with great heat and light, *combustion* is said to occur. In order to start the process, it is generally necessary to heat the body; afterwards the heat given out by the chemical change produced is more than enough to carry it on, and the combination goes forward with increasing vigour until it is completed.

Bodies which are burned, and which disappear from sight—as when coal or charcoal is consumed in the fire—are in no case actually destroyed. They are only altered in form. A candle, for example, in burning seems to be completely consumed, but the materials of which it consisted are not destroyed. This most important fact may be proved as follows :—

Exp. 17.—Take a glass tube 30 or 40 centim. long and 4 cm. in diameter. Thrust a piece of wire gauze half-way down the tube, and fill the upper half with fragments of caustic soda (Fig. 7). To the lower end of the tube fit a cork pierced with three or four holes for the admission of air, and fasten to it a short piece of wax taper. To the other end of the tube fit a cork through which a short tube of about 8 millimetres in diameter is passed. Now weigh the tube and its contents. By means of a piece of india-rubber tubing, join the short tube at the top with a closed jar filled with water, which is to act as an aspirator. This is easily made from a tinplate 9-litre (2-gallon) oil can, into the side of which, near the bottom, a small cock is soldered. Open the stop-cock near the bottom of the closed jar, and let

the water flow. The water cannot run out at the stop-cock unless air takes its place; and since the aspirator is connected by the caoutchouc tubing with the wide glass tube, which is open freely to the outer air at the bottom, a current of air is established through the wide tube. Now withdraw the cork at the bottom, light the taper, and immediately put it back into the

Fig. 7.



tube. In three or four minutes' time close the stop-cock: the taper will at once go out. When the apparatus is cold, slip off the caoutchouc connecting tube, and weigh the wide glass tube. It will be found to have gained in weight by several decigrams.

The candle in burning combines with a portion of oxygen from the air, forming water and carbonic anhydride. These are both absorbed as they pass over the caustic soda, and hence, though the taper itself looks smaller, and has really lost in weight, the chemical products obtained weigh more than the taper originally did.

Whether a body be burned quickly or slowly, the quantity of heat which a given weight of it, say, 1 gram, gives out in burning is perfectly fixed, and depends upon the nature of

the burning body. Nevertheless, the more the oxygen is diluted by mixture with a gas which does not act chemically upon it, such as nitrogen, the lower is the apparent temperature which is produced at the moment by combustion; because not only are fewer particles of oxygen in contact with the burning body, but at the same time the diluting gas carries off part of the heat, since it has its own temperature raised without contributing to the chemical action. And hence, when a body is burned in air, it seems to give out much less heat than when burned in oxygen, and it burns much more slowly. But when we blow a fire with the bellows, or cause a powerful draught of air up the chimney, we quicken the combustion and raise the heat, because we thus bring a larger number of particles of oxygen into contact with the fuel in a given time; and by the same operation we carry off the gases formed by combustion, which are unable to combine with the burning body, and would prevent its contact with fresh particles of the oxygen of the air. That this is so may be seen by the check to the fire and the reduced consumption of fuel caused by closing the damper or shutting the ashpit door of a furnace.

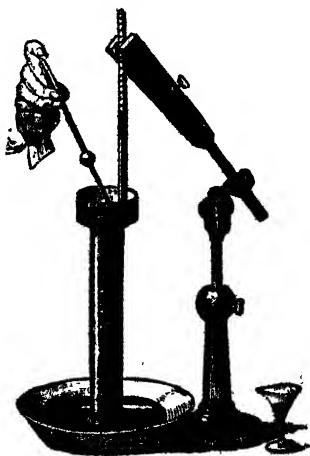
Oxygen is the most important and also the most abundant of the elements. We have already seen (Exp. 5), that it forms a little more than a fifth of the bulk of the air; it also constitutes eight-ninths of the entire weight of water; while clay, limestone, and siliceous sand contain about half their weight of it. Oxygen is also found largely in various other common substances not of mineral origin, such as sugar, starch, and woody fibre, which contain about half their weight of it; and many bodies derived from animals, such as muscular tissue, leather, and horn, contain it in large proportion.

Oxygen may be shaken up with water without experiencing any sensible change in bulk, for it is only slightly soluble in that liquid, 100 cub. centim. of it, at 15° C., dissolving about

3 c. c. of the gas; but this solubility, slight as it may appear, is essential to the existence of living animals, for it is only in the dissolved state that the gas finds its way into the blood, and effects the chemical changes in the body necessary to life, both in land animals and in those which live in water. A solution of potash may also be shaken up with oxygen without sensibly dissolving it; but if pyrogalllic acid be added to the potash solution, the oxygen is rapidly absorbed, and the liquid turns brown.

Exp. 18.—Pass a few bubbles of oxygen into a strong tube, graduated to divisions of 0.5 c. c. each, filled with mercury, and placed in a deep glass full of mercury (Fig. 8). Introduce a solution of potash (1 part of solid potash in 4 of water) by means of a pipette with a point curved upwards, blowing into the pipette with sufficient force to drive over 8 or 10 drops of the solution. Agitate this liquid briskly with the gas by thrusting the tube down quickly into the mercury, and raising it to its former level several times. The oxygen will not alter in volume. Now, with a *fresh* pipette, introduce an equal quantity of a solution of pyrogalllic acid (1 part of acid and 6 of water). Again agitate the mixture. It becomes intensely brown, and the whole of the gas will disappear if pure. If a measured quantity of air be taken, it is easy in a few minutes to ascertain roughly the proportion of oxygen present by the absorption effected in this way, because the nitrogen is left unchanged, and may be measured after the absorption of oxygen is over.

Fig. 8.



Oxygen is a little heavier than atmospheric air. A measure of air which weighs 1 gram would, if filled with oxygen at the same temperature, and when the barometer stands at the same height, weigh 1.1056 gram; and a measure of hydrogen which weighs 1 gram would, when filled with oxygen, weigh exactly 16 grams: so that oxygen is precisely 16 times as heavy as hydrogen.

(10) *Measurement of Gases under Standard Conditions.*—It is necessary when comparing the weights of gases with each other to attend carefully to the temperature. A quantity of any gas which at 0° C. exactly fills 1 litre expands so rapidly when heated, that at 273° C. it would become dilated to 2 litres. A quantity of any gas which at 0° C. measures just 1 litre would, if heated to 100° C. (the temperature of boiling water), become expanded to 1.366 litre. It is now customary to compare gases at the standard temperature of 0° C.; or, if they are not actually at this temperature, to reduce the results to this point by calculation. For instance, if v be the volume of any gas measured at the temperature t in Centigrade degrees, and V be the bulk of the same gas at 0° C., then—

$$V = \frac{273 \ v}{273 + t}.$$

It is equally important to compare gases at a fixed barometric pressure. At the level of the sea, the average weight of a column of air which reaches to the top of the atmosphere will exactly balance a column of mercury 760 millimetres high, and at 0° C. But at the top of a mountain of a little more than 5.5 kilometres or nearly 3.4 miles high, the weight of a column of air reaching to the top of the atmosphere would only be able to balance a column of mercury of half this height, or 380 mm. And a quantity of air at the bottom of the mountain which measures 1 litre while the barometer stands at 760 mm. would, if carried to the top of the mountain, expand to 2 litres. But it is not necessary to take the air to the top of the mountain in order to observe this fact:

for if the pressure upon the gas be by any other suitable means lessened to one-half, the air will immediately become doubled in bulk. If, on the other hand, the pressure be doubled, the air will become reduced in bulk to one-half. Gases, in fact, occupy a space inversely as the pressure to which they are subjected ; and, in order to avoid inaccuracy in measuring them, they are always compared by calculating them as if subjected to a fixed or standard pressure of a column of mercury at 0° C. of 760 mm. high.

Suppose v to be the observed volume (after it has been corrected, if necessary, for temperature), p the pressure at the time of observation, measured by the height of the mercurial column in the barometer in millimetres, and V the volume corrected to the pressure of 760 mm. of mercury, then—

$$V = \frac{p v}{760}.$$

In taking the specific gravity of gases, it has been the practice to compare them with an equal bulk of dry air as the standard. When, for instance, it is said that the specific gravity of oxygen is 1.10563, the expression means that if a vessel which holds a certain volume of dry air which weighs exactly 1 gram, were filled with dry oxygen gas, at the same temperature and pressure, the weight of this oxygen would be 1.10563 gram ; the same bulk of dry hydrogen would be only .0691 gram, and the specific gravity of hydrogen is said to be .0691.

This practice of comparing gases with air is both customary and convenient ; but it has been objected to on the ground that air is a mixture, and not a true chemical compound. Now the proportions of the substances in a mixture are liable to variation, while those of a chemical compound are invariable. Fortunately for the accuracy of the data founded on comparison with the air as a standard, the proportions of the oxygen and nitrogen in the air do not vary practically to any important amount, but the objection in

principle remains. Hence it has of late years become the custom further to compare the weights of gases and vapours with the weight of an equal volume of some elementary body ; and the element selected for the purpose is hydrogen, the lightest of all known substances. The result of this comparison with hydrogen will hereafter be spoken of as the *relative weight* of a gas or vapour. Suppose that, for the purpose of this comparison, we take a vessel which would hold 1 gram of hydrogen at 0° C. and 760 mm. barometer ; the capacity of such a vessel would be 11.19 litres. This measure, when filled with oxygen under similar circumstances, would contain 16 grams of oxygen ; and if filled with nitrogen, it would contain 14 grams of nitrogen. Hence, if the weight of such a bulk of hydrogen be called 1, the relative weight of oxygen will be 16, the relative weight of nitrogen 14, and so on.

(11) *Acids, Bases, and Salts.*—The compounds formed by the union of oxygen with the other elements differ from each other very much in properties ; but among them are two important classes of oxides, chemically opposed to each other, one commonly, but erroneously, known as acids, the other as bases. Everyone is familiar with the sourness of vinegar or of a lemon, which in both cases is due to the presence of a substance known in chemical language as an *acid*. The acetic acid gives the sour taste to vinegar ; the citric acid is the substance which gives the sharp flavour to the lemon. There are many other well-known substances, like sulphuric, nitric, and phosphoric acids, which when diluted sufficiently to prevent them from injuring the surface of the tongue, possess a sour taste ; and these all belong to the class of acids.

Again, most persons are acquainted with the nauseous taste of soda, and with the peculiar soapy feeling which it occasions when rubbed upon the skin : this is due to what is called the *alkaline property* of soda, a property in which it resembles potash, and a few other substances. The alkalis are soluble in water, and form one class of a numerous group of chemical agents, known under the name of bases.

Many elementary substances, like sulphur and phosphorus, by their combination with oxygen, furnish compounds which are freely soluble in water, and have a sour, and often a burning taste; they also turn many vegetable blue colours, such as the blue of an infusion of litmus,* or of purple cabbage, to a bright red. Such oxides are called *anhydrides* (which means bodies free from hydrogen) to distinguish them from the bodies these same oxides furnish when they are acted upon by water, which all contain hydrogen, and belong to the class of *acids*. All the non-metallic elements, except hydrogen and fluorine, form with oxygen one or more compounds, which, when dissolved in water, produce acids, and often intensely powerful acids. Many of the metals, on the other hand, by their union with oxygen, give rise to bodies of an opposite kind, which have been termed *bases*. For instance, the white alkaline substance formed by burning potassium in oxygen is dissolved rapidly by water; it produces a colourless liquid, of a soapy, disagreeable taste, and a peculiar lixivial smell. It corrodes the skin, dissolves oil-paint, restores the blue colour to litmus which has been reddened by an acid, and *neutralises* the strongest acids. This power which acids and bases have of reacting upon each other, and destroying the chemical activity which each has when separate, is the most marked feature of these two classes of substances. The compounds produced by their action upon

* Paper tinged blue with a watery or spirituous infusion of litmus (a colouring matter obtained from certain lichens) is in constant use for showing the presence of an acid in a liquid, as it immediately becomes reddened by the action of even very small quantities of an acid when uncombined with a base. The same paper, if faintly reddened by means of vinegar or any other acid, is equally valuable as a *test* for an alkali, which if present uncombined with acids immediately restores the blue colour. The alkalies also turn paper tinged yellow with the colouring matter of turmeric or rhubarb to a reddish-brown hue.

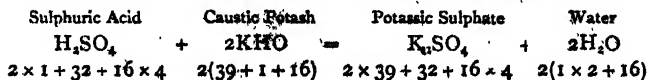
A *test* in chemistry simply means a method of trial, and *test* solutions or *test* papers, are solutions or papers made for the purpose of trying whether certain substances are present or not, according as the solution or paper does or does not undergo a particular change, which would be produced if the body sought for were there.

each other constitute what are called *salts*, and, when freed from the water in which they are dissolved, may often be obtained in crystals.

Exp. 19.—Cut a red cabbage into slices, and boil it with water; strain off the purplish liquid thus obtained. To a portion of this decoction add a little solution of caustic potash: a green liquid will be produced. To another portion of the cabbage liquor add a few drops of sulphuric acid: the solution will become red. Pour the red acid liquor into the green alkaline solution, and stir the mixture: the red colour at first disappears, and the whole remains green; but on continuing to add the red liquid cautiously, a point is reached at which the liquid assumes a clear blue colour. There is then no excess either of acid or of alkali in the solution; and on evaporating the liquid a neutral salt, *potassic sulphate*, formed by the action of the acid upon the alkali, may be obtained in the form of crystals.*

Here it is necessary to remark that the same element often forms more than one oxide which when dissolved in water, furnishes an acid. When this is the case, the oxide which contains the largest quantity of oxygen is designated by a name ending in *ic*, while the compound with the smaller proportion of oxygen is made to end in *ous*. Sulphur, for example, furnishes both *sulphuric* acid (H_2SO_4) and *sulphurous* acid (H_2SO_3); and both these acids form salts when acted upon by bases. The salts of acids ending in *ic* are indicated by names which end in *ate*, while the salts of acids in *ous* have names ending in *ite*. For instance, the salts of sulphuric acid are called sulphates; of nitric acid, nitrates; of phosphoric acid, phosphates; while those of sulphurous

* The change may be expressed in symbols in this manner:—



from which, by reference to the table of atomic weights (page 5), it may be seen that 98 grams of pure sulphuric acid, with 112 grams of caustic potash, would form 174 grams of a neutral salt, and would set free 36 grams of water.

acid are called sulphites; those of nitrous acid, nitrites; and of phosphorous acid, phosphites.

The acids are not all soluble in water; and the insoluble acids have no sour taste. In like manner bases exist, such as zinc oxide and ferric oxide, which are not soluble in water, and then they neither corrode the skin nor exert any sensible effect upon coloured tests; but they are capable of reacting chemically with acids, and forming salts.

Exp. 20.—Add zinc oxide to diluted sulphuric acid and stir the two together: it will be readily dissolved, and, on evaporating the liquid, a true salt, zinc sulphate, may be obtained in needle-shaped crystals:—



Sometimes the same metal, when combined with different quantities of oxygen, furnishes two different bases, or bodies capable of neutralising acids more or less completely. Iron, for instance, furnishes *ferric oxide* (Fe_2O_3) and *ferrous oxide* (FeO); mercury also gives mercuric oxide (HgO) and mercurous oxide (Hg_2O). The base to which the name ending in *ic* is given always contains the larger proportion of oxygen. A compound formed by the action of ferrous oxide on sulphuric acid would be called *ferrous sulphate*; while that furnished by the action of ferric oxide on sulphuric acid would be known as *ferric sulphate*.

Besides the oxides which furnish acids and bases, there is a third set of oxides, which is neither acid nor basic, and is not disposed to enter into combination with either class. Black manganese oxide (MnO_2); or, as would be better, by doubling the molecular formula, MnO , MnO_3 , magnetic iron oxide (FeO , Fe_2O_3), and red lead (2PbO , PbO_2), afford instances of this kind. Such oxides appear generally to be formed by the union of two different oxides of the same metal with each other, and are analogous to salts. Indeed, the union of an anhydride with an anhydrous (or water free)

basic oxide furnishes a true salt; for instance, sulphuric anhydride (SO_3), by uniting with cupric oxide (CuO), furnishes cupric sulphate (CuO, SO_3 , or CuSO_4 , as it is usually written); but in such cases no separation of water occurs.

(12) *Ozone*.—Oxygen in its usual form has no sensible smell, but it may be obtained in a more active condition, and then it has a very peculiar odour. This smell is perceived whenever an electrical machine is put in action in the air, and more or less ozone (as it has been called from the Greek $\delta\zeta\omega$, I smell) is immediately produced. It is also formed whenever water is decomposed between platinum plates by the voltaic battery (p. 44). A special form of apparatus has been contrived for electrifying a current of air, so as to change part of its oxygen into ozone. Ozone may also be obtained by chemical means.

Exp. 21.—Scrape off the white coating of a stick of phosphorus under water, and cut the cleansed phosphorus into pieces 12 or 15 millim. long. Place one of these pieces in a wide-mouthed litre bottle full of air, with about a teaspoonful of water at the bottom. Close the mouth of the bottle with a glass plate, and expose the whole for half an hour to a temperature of 15° or 20° C. Then invert the neck of the bottle in water, and allow the phosphorus to fall out. Replace the glass plate, and withdraw the bottle and its contents from the water. The phosphorus in this experiment undergoes a slow oxidation, during which a little ozone is formed, and is left mixed with the air; but the ozone will be again destroyed if it is left too long with the phosphorus.

The most delicate test of ozone is potassic iodide (KI), from which it immediately sets iodine free, which can instantly be detected by its action on starch.

Exp. 22.—Boil a gram of starch in 50 grams of water, so as to produce a thin mucilage, and add 0.1 gram of potassic iodide to the mixture. Brush a little of this solution over a slip of clean writing-paper, and plunge the paper into one of the jars in which the phosphorus has been acting on the air. An imme-

•
diate blue stain is produced, owing to the action first of the ozone upon the iodide, and then of the free iodine upon the starch. Paper may be prepared beforehand with this starch paste and iodide, and dried; in which form it may be kept in a bottle till wanted.

The ozone displaces iodine from the iodide, though ordinary oxygen will not do so.

The slow oxidation of ether, of oil of turpentine, and of many other substances, is attended with the formation of small quantities of ozone; and most plants, when growing in the sunshine, give it out in excessively small quantities. Traces of ozone are probably present usually in the air, but the proportion varies. If a piece of the dry iodized paper be exposed for five minutes in the open air of the country, it acquires a bluish tint, the strength of which varies on different days, according as the quantity of ozone in the air is greater or less. Sometimes, in damp or foggy weather, no such change occurs, and it is scarcely ever observed in the air of large towns. The effect is most marked on the sea coast, and when the wind blows off the sea. It is not improbable that these minute quantities of ozone exert an important purifying effect upon the atmosphere by destroying and oxidising animal effluvia, which would otherwise increase in quantity until they produced disease. The ozone is absorbed by these offensive bodies, which it converts into harmless compounds.

Ozone is not soluble in water, but it at once corrodes caoutchouc, cork, and many other organic matters. It produces a feeling of irritation in the lungs when air strongly charged with it is breathed. It immediately oxidizes the common metals, as well as mercury when dry, and even silver, if it be moist. It is instantly changed into common oxygen, if passed over manganese oxide, on which, however, it produces no permanent effect. Several other bodies also on which it exerts no sensible action change it into common oxygen; and if it be heated to a temperature not greater

than that of boiling water, a similar change occurs. Ozone is much denser than oxygen gas : probably three measures of oxygen furnish by condensation two measures of ozone. The exact amount of condensation, however, is not certain, because ozone has never been obtained free from admixture with a very large proportion either of air or of oxygen.

Ozone has a powerful bleaching action. It has been attempted to make ozone by electric action on the air, and to use the product as a bleaching agent.

Exp. 23.—Take a bottle of air which has been ozonised by means of phosphorus, and add to it a few drops of a *very* dilute blue solution, formed by dissolving powdered indigo in strong sulphuric acid, and then diluting it with water. If the blue liquid is shaken up with the ozonised air, the colour quickly disappears.

The mode in which electricity and phosphorus, and other agents, act upon oxygen and convert it into ozone is not understood.

(13) NITROGEN: *Symbol* N; *Atomic Wt.* 14; *Atomic Vol.* \square ; *Sp. Gr.* 0.971; *Rel. H₂.* 14; *Mol. Wt.* N₂, 28; *Mol. Vol.* \square .

The most abundant constituent of the atmosphere, nitrogen (the 'generator of nitre,' so called because it is an essential component in nitre) is also sometimes called *azote*, because it is unfit to support life.

The easiest methods of obtaining nitrogen are founded upon the removal of oxygen from the air. One of these, the exposure of moistened iron filings to air contained in a jar over water, has been already described (*Exp. 4*).

Exp. 24.—Support a stick of phosphorus upon a wire above the surface of a dish of water, and place a jar of air over it. The phosphorus will, without the aid of heat, gradually remove the oxygen from the air, forming phosphorous anhydride (P₂O₃), which will be dissolved by the water, and in a day or two the gas which is left will be nitrogen nearly pure.

Exp. 25.—The same change may be effected in a few minutes if the phosphorus is heated. Dry two or three pieces of phosphorus of the size of a pea upon blotting-paper, and float them in a small porcelain dish upon the water in the trough: kindle the phosphorus by touching it with a hot wire, and cover it at once with a jar full of air. The phosphorus will burn till it has exhausted all the oxygen in the jar, which will become filled with white fumes of phosphoric anhydride (P_2O_5). These become gradually dissolved by the water, and nearly pure nitrogen is left.

Oxygen may also be very completely separated from nitrogen by allowing the air to stream very slowly over finely divided copper made red hot.

Nitrogen has neither colour, taste, nor smell. It has never been liquefied by cold or pressure. It is a little lighter than air. A measure of hydrogen which would weigh 1 gram would, when filled with nitrogen at the same temperature and pressure, weigh 14 grams. Water dissolves it but sparingly, taking up about one-fiftieth of the bulk of the gas. Nitrogen alone is unfit for the support of life, but it is not a direct poison, and is, indeed, constantly inhaled when mixed with oxygen, the activity of which it serves to moderate.

Exp. 26.—Plunge a lighted taper into a jar of nitrogen: the gas does not take fire, but the light is put out instantly.

Nitrogen offers a striking contrast in properties to oxygen. It has scarcely any tendency to unite directly with any of the elements except boron, titanium, and one or two of the rarer metals. Yet it is one of the most widespread forms of matter; it is found in the free state in the air, as well as in combination in some of the most active and important compounds—such, for instance, as in nitric acid, which is obtained from the nitre of commerce, and in ammonia or hartshorn. Though not abundant in plants, it is never quite wanting in them. It also forms part of the strongest vegetable poisons and medicines, such as prussic acid, strychnia, and morphia; and it is a component of some of the most important

articles of food, such as bread, milk, and the flesh of animals. The compounds which nitrogen forms with each of the other elements are called *nitrides*, and animal substances which contain nitrogen are often spoken of as *azotised* substances.

(14) *Air a Mixture of Several Gases.*—

Exp. 27.—Measure off into a jar over water 210 c. c. of oxygen, and add to it 790 c. c. of nitrogen; then introduce a lighted taper. It will continue to burn as in ordinary air.

Such a mixture might be breathed with perfect safety, and would possess most of the properties of the air. The atmosphere is in fact a true mixture of several gases, among which nitrogen and oxygen are by far the most abundant. Though these two gases are not chemically united in the atmosphere with each other, yet in the open air they are found to be mixed in very uniform proportions. Careful analyses of numerous specimens of air taken from the most distant parts of the earth furnish results the extremes of which do not vary from one another in the proportion of oxygen more than about 1 part in 200, and generally the variation is much less. The samples were taken, amongst other places, from Port Bowen, amidst the perpetual ice of the Arctic Circle; from Vera Cruz, the hotbed of yellow fever; from the summits of the Andes in the western hemisphere, and of the Alps in the eastern; from the higher regions of the atmosphere in balloons, as well as from the streets of the crowded capitals of Europe, such as London, Paris, Berlin, and Madrid. Supposing all the ingredients of the air except nitrogen and oxygen to have been removed by proper means, it has been found that 1 litre, or 1000 c. c., of the mixture would contain on the average 209.5 c. c. of oxygen and 790.5 c. c. of nitrogen. If the quantities be determined by weight, instead of by measure, 1000 grams of the mixture would contain 232.2 grams of oxygen and 767.8 grams of nitrogen.

- But it is easy to show that air always contains other substances besides oxygen and nitrogen.

Exp. 28.—Pour a little clear lime-water into a saucer, and leave it for a few minutes. A white skin or film will gradually be formed upon the surface, and this if shaken will sink to the bottom; a fresh film will then be formed in its place, and if this be disturbed it will again be renewed, until the whole of the lime has been separated from its solution in the form of this white substance, which has the chemical composition of chalk, or calcic carbonate.

In this experiment the lime has taken up from the air one of the less abundant gases which it contains, and to this gas the name of carbonic acid or carbonic anhydride (CO_2) has been given. The quantity of this gas is always small. It varies in 1 litre, or 1000 c. c., of air from 0.3 to 0.6 c. c., so that 10,000 measures of air contain from 3 to 6 measures of this gas.

Exp. 29.—Pour some water into a glass tumbler, taking care to keep the outside dry; place in the water a lump of ice. In the course of a few minutes the water will have become cooled by the melting ice, and the cooling effect will extend to the outer surface of the glass, while dew or moisture will be deposited upon it, owing to the condensation of viewless watery vapour from the air.

This experiment shows the presence of steam in the atmosphere. The proportion of watery vapour, however, varies greatly from time to time, being much less during the frosts of winter than it is in the hot weather of summer. In this climate 1000 c. c. of air seldom contain more than 20 c. c. of invisible vapour, and the proportion ordinarily found in a litre, or 1000 c. c., may be roughly reckoned at 14 c. c.

The weight of a litre of dry air free from carbonic anhydride, at 0°C . when the mercury in the barometer stands at 760 mm., has been found to be 1.2932 gram.

It must also be added that variable traces both of ammonia and of nitric acid are found in the air, but the pro-

40 *Less abundant Components of Atmospheric Air.*

portions are so minute that they cannot be detected unless very large quantities of air are examined; and these substances are more easily found in the rain, which, by falling through large tracts of air, has dissolved them, and brought them down with itself. Minute as the quantity is which is found even then, they have important uses in supplying what is needful for the health of growing plants.

In large towns small quantities of other gases are likewise occasionally met with, such as sulphurous anhydride (SO_2), derived from the pyrites in the coal consumed, and sulphuretted hydrogen (H_2S), from the putrefaction of animal refuse.

Besides these gaseous bodies, minute particles of solid matter are always suspended in the air; these are of the most varied kinds, and among them are the spores and seeds of minute fungi and plants. These particles are so small that they commonly escape notice; under favourable circumstances they may be easily seen, as they form the 'motes' which appear to be dancing in the sunbeams when they find their way into a darkened room.

The average composition of a litre, or 1000 c. c., of air may be represented as follows, in measure of each ingredient:—

	Cub Centim.
Oxygen	206·1
Nitrogen	779·5
Aqueous Vapour (about) . . .	14·0
Carbonic Anhydride	·4
Nitric Acid	} . . traces
Ammonia	
Carburetted Hydrogen . . .	

	1000·0

CHAPTER III.

WATER—HYDROGEN.

(15) WATER : *Symbol*, H_2O ; *Atomic and Mol. Wt.* 18 ; *Sp. gr. of liquid at 4° C.* 1.000 ; *Sp. gr. of ice*, 0.918 ; *Sp. gr. of steam*, 0.622 ; *Rel. Wt.* 9 ; *Atomic and Mol. Vol.* .

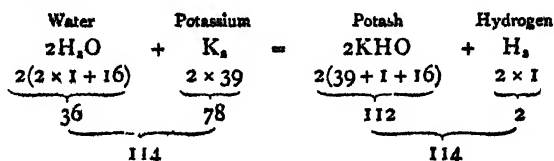
Until about a hundred years ago this wonderful and universally diffused liquid was, like the air, supposed to be one of the elements of nature ; but we can now easily prove that it is a compound body, and can both separate it into its elements, and reproduce it from those elements by causing them again to combine together.

Exp. 30.—Throw a small piece of the metal potassium into a saucer containing water, and retreat to a little distance. As the metal is lighter than water, it will rise to the surface, where it will seem to burst into flame, rolling rapidly about until it disappears with a slight report. Now place a piece of reddened litmus paper in the water : it will become blue, showing that the potassium has combined with oxygen, which, as we shall see, is derived from the water, and has been by it converted into the alkaline body potash (*Exp.* 16).

Exp. 31.—Roll upon the end of a cedar pencil a piece of wire gauze about 4 centim. square, and fold up the end of the cylinder thus formed ; twist a piece of copper bell-wire 25 or 30 centim. long round the little cage, so as to form a handle ; then introduce into it one or two small pieces of sodium, the metal contained in common salt, and pass the cage quickly beneath the mouth of a small glass jar filled with water, and inverted in water : bubbles of gas will be formed at once, and will continue to rise into the jar until all the sodium has disappeared. Now close the jar with a glass plate, withdraw it from the water, and apply a light. The gas will take fire, and burn with a pale flame.

To this substance the name of *hydrogen* (water-producer) has been given. It is regarded as an elementary body.

The results of these experiments may be thus explained :
 Water is a compound of oxygen and hydrogen. The potassium or the sodium displaces a part of the hydrogen from the water, forming potash or soda, which is dissolved by the water, while the hydrogen escapes in the gaseous form, as may be explained by the following equation :—



When potassium is used, the hydrogen becomes so much heated at the moment when it is set free that it takes fire in the air at once ; but when the sodium is kept under water, the hydrogen is prevented from mixing with the air till it becomes cool, and then it does not burn till a light is applied to it.

Fig. 9.



If a small voltaic battery can be had, it is easy to obtain both the oxygen and the hydrogen from the water at the same time.

Exp. 32.—Select two pieces of glass tube of equal diameter, about 12 centim. long and 12 mm. wide, and open at both ends. Fit a cork into one end of each, and pass a stout platinum wire, ending in a small plate of platinum, through each cork, so as to reach nearly to the open end of the tube. Then cover each cork neatly with a solution of sealing-wax in spirit of wine, and let it dry. Next fill each tube with water slightly acidulated with sulphuric acid* (about 1 part of acid in 30 of water), and invert it in

* Much heat is given out whenever strong sulphuric acid is mixed even with cold water. When this mixture is to be made, the water

a glass of the same acidulated water (Fig. 9). Connect one of the platinum wires with the wire proceeding from one of the poles of a properly charged voltaic battery, which may consist of three or four cells made on Grove's plan (see treatise on 'Electricity'), and connect the other platinum wire with the remaining pole of the battery. Gas will begin at once to rise from both plates, and will collect in the tubes: one of these tubes will receive just twice as much gas in the same time as the other. When sufficient gas has been collected, remove the tube with the smaller quantity of gas, closing it with the thumb before lifting it out of the water. Turn it mouth upwards, and introduce a splinter of wood red-hot at the point. It will be rekindled. This we know is a characteristic property of oxygen. Now remove the other tube in a similar manner, and apply a lighted taper. The gas will take fire, and burn with the pale flame peculiar to hydrogen.

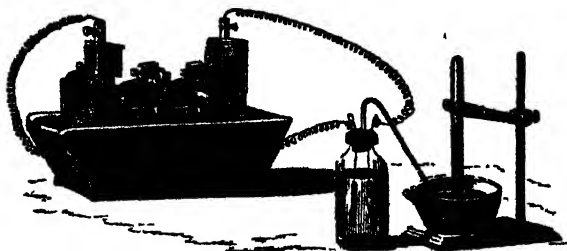
In this experiment it is to be noted that for each cubic centimetre of oxygen obtained from the water 2 c. c. of hydrogen have been procured. Further, it may be easily shown that these two gases may be made to combine again chemically in the same proportions, and that they then reproduce water. For this purpose the last experiment must be altered in form as follows:—

Exp. 33.—Fit a good cork to the neck of a bottle which will hold 100 c. c., adjust a tube, bent as in Fig. 10, to the cork, having its lower end turned upwards, and pass the wires connected with the two platinum plates through the cork, taking care that the metals do not touch each other. Nearly fill the bottle with water slightly acidulated with sulphuric acid, and insert the cork with its bent tube and platinum plates. Connect each plate with one of the wires of the voltaic battery, as before; allow the air in the tube to be displaced by the gas, and then collect the mixed gases, as they rise from both plates, in a strong

should be placed in a jug or earthenware vessel; it should be stirred round and round with a glass rod, and the acid should be poured into the water (not the water into the acid) in a slender stream, the whole being kept stirred till the mixture is complete.

dry tube filled with mercury, and supported in a wooden vice, and inverted in a small Wedgwood-ware mortar containing mercury. When the tube has become full of gas, close the end of it with the finger, raise it out of the mercury, and apply a light :

Fig. 10.



a sharp report will be heard ; the two gases will suddenly unite, and the sides of the tube will become dewed with moisture, showing that water has been formed by the union of the oxygen and hydrogen.

Another mode of making this important experiment will be described when we come to treat of hydrogen.

Each litre of oxygen gas unites with exactly two litres of hydrogen ; and if the gases be heated to above 100°C . before causing them to unite, and the heat be kept up to the same point after they have united, exactly two litres of steam or watery vapour will be obtained. Hence, in representing the composition of water by symbols, its formula is written H_2O , and its combining number is 18. When converted into vapour 9 grams of water furnish a bulk of steam exactly equal to that of 1 gram of hydrogen at the same temperature and pressure ; so that the *relative weight* of steam is 9, and the specific gravity of steam is 0.622 ; or the weight of a quantity of steam, compared with that of a quantity of air which weighs 1 gram at the same temperature and pressure, is 0.622 gram. It is also convenient to bear in mind that 1 litre of water will at 100° furnish 1696 litres of steam. of

an elasticity sufficient to balance the pressure of a column of mercury of 760 millimetres, 1 cubic inch of water producing nearly a cubic foot of steam.

Pure water has neither taste nor smell, and it is generally supposed to be colourless, though when seen through a depth of 5 or 6 metres it has a delicate and faint tinge of blue. When cooled sufficiently, it becomes converted into the transparent solid form of ice. The point at which pure ice melts, or the *freezing point*, as it is usually called, always occurs at exactly the same temperature, if the ice is not exposed to pressure. Hence the melting point of ice has been made the starting point or 0° , the zero, as it is termed, of the centigrade thermometric scale.* Again, if the temperature of water be raised sufficiently high, the liquid assumes the form of gas, while bubbles of steam rise through the heated liquid and break upon its surface, passing off as invisible vapour. The water is said to boil, and its vapour is then of an elastic force just sufficient to balance the pressure of the air upon its surface, whatever that pressure may be. The temperature at which pure water boils under equal pressures is found to be quite as uniform as its freezing point. This *boiling point* of water serves, therefore, as a second fixed point upon the thermometric scale, and it has been agreed to call the point at which the mercury stands in boiling water 100° on the centigrade scale; the observation being always made when the pressure of the air upon the surface of the boiling water, as indicated by the barometer, is equal to that of a mercurial column 760 mm. long when measured at 0° C. One degree of the centigrade scale represents the 100th part of the apparent expansion of the mercury in the thermometer between the freezing and the boiling points of water.†

* If the water holds salts dissolved in it, the freezing point is lowered to an extent depending on the quantity and kind of salt.

† If salts are present in the water, the boiling point may be raised several degrees, the amount varying according to the quantity and kind of salt in solution.

But water *evaporates*, or slowly passes off into the air in the invisible form of vapour or steam at all temperatures—even from ice itself; and this evaporation is going on more or less actively almost everywhere upon the surface of the earth, so that the air is at all times charged with moisture, the proportion of which is perpetually varying. In dry weather the quantity of vapour found is always less than that which could exist unseen in the air at the time. It is owing to this circumstance that wet bodies, when exposed to the air, become dry in a few hours. By the process of evaporation from the surface of the land, as well as of the ocean, a natural distillation and purification of water, of the utmost importance, is always taking place around us. The water discharged by rivers into the sea returns unperceived into the air. The vapour is at first unseen, but as it rises into the colder regions of the atmosphere it is condensed into masses of visible cloud. These at last become too heavy to stay aloft. High ridges or mountains are especially active in arresting the clouds, which then fall in showers, and supply the high lands with water. This flows down the sides of the hills, collects into rivulets, and these again into rivers; or else the water sinks into the earth through the porous strata, and passes down until it meets with a bed of clay or some stratum through which water cannot pass. The liquid, when thus stopped, flows along over the face of the imbedded stratum until it reaches the surface of the soil at some lower level in the valley, where it bursts forth in the form of a spring.

Water exhibits a remarkable exception to the law of contraction by the removal of heat, which all other bodies obey. When exposed to a falling temperature, it diminishes in bulk regularly till it has become cooled down to 4°C .; and then, instead of contracting, it begins slowly to expand, and continues to do so until it reaches the freezing point, when the ice which is formed suddenly expands still more. This exceptional expansion of water as it cools is attended with

very important consequences to our well being. During the frosts of winter a rapid process of cooling occurs from the surface of all lakes and streams; the colder water sinks to the bottom until the whole has become reduced to $4^{\circ}\text{C}.$, but below this point the colder water becomes the lighter, and remains at the top, so that it protects the mass beneath from the winter cold. In this way it prevents such a reduction of temperature in deep pools as would be fatal to fishes and aquatic animals. The ice also floats upon the surface, and thus the bottoms of lakes and rivers are preserved from the accumulation of masses of ice, which, if it sank as fast as it is formed, could never be melted even by the summer's sun.

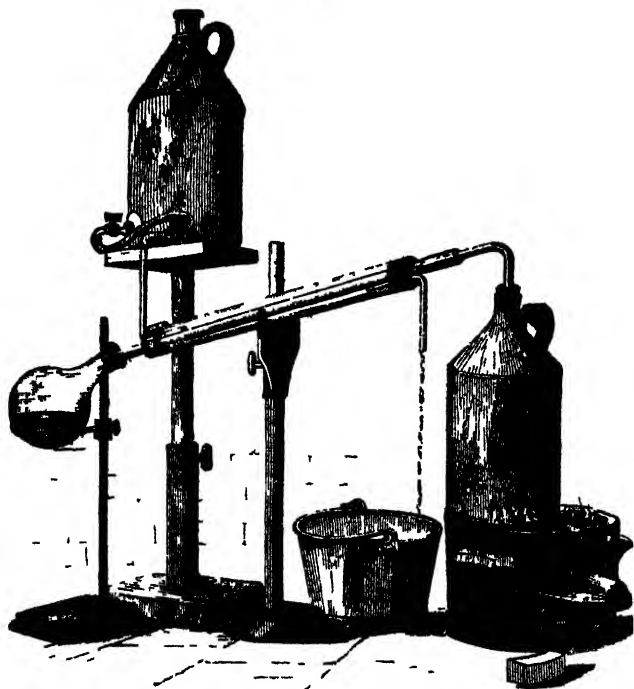
The temperature of $4^{\circ}\text{C}.$ is that at which water is heavier than at any other, and is hence called its point of *maximum density*. A litre of water at this temperature weighs exactly 1000 grams, or 1 kilogram. Water is 773 times as heavy as air at $0^{\circ}\text{C}.$, when the barometer is at 760 mm. In taking the specific gravity of solids and of liquids, they are always compared with the weight of an equal bulk of pure water at $4^{\circ}\text{C}.$ For example, if gold be said to have a specific gravity of 19.34, it is meant that 1 c. c. of water at 4° weighs 1 gram, while a cub. centim. of gold at the same temperature weighs 19.34 grams.

In order to obtain pure water for this and various other purposes, it must be distilled. This is usually performed by means of a still and worm-tub; but if these be not at hand, a small quantity of water may be distilled in the following manner:—

Exp. 34.—Procure a clean tinplate 9-litre (or 2-gallon) oil can; bend a glass tube into the form shown in Fig. 10; adapt it to a sound bung which exactly fits the neck of the can, and fill the can about two-thirds full of water. Then adjust the bent tube to the condenser shown in the figure. Place the can upon the fire, and heat it till the water boils steadily, whilst a small stream of cold water is kept running through the outer tube of the

condenser. Allow the water as it distils over from the can to flow into a flask placed for its reception. Throw away the first 40 or 50 cub. cm., which are apt to contain a little ammonia and semi-gaseous impurities. Then collect 3 or 4 litres. This will be *distilled water*; and if the experiment is performed carefully,

Fig. 11.



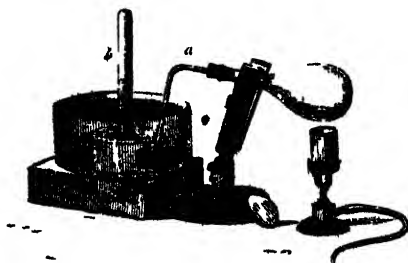
the liquid so condensed will be pure from all solid substances in solution. A few drops when allowed to evaporate from a slip of clean glass will leave scarcely a perceptible mark behind; but if a few drops of the water before distillation be so treated, a distinct residue will be obtained. A sufficient condenser may be made without difficulty as follows:—Select a piece of glass tube

of about 80 centim. in length and 2 centim in diameter; fit it by means of corks into a second tube of glass or of tinplate about 60 centim in length and 4 centim. in diameter. Into the space between the two tubes pass a bent quill tube through one of the corks, and introduce through the other cork a second similar tube, cold water is to be supplied through the tube at the lower end, while the hot water runs off at the upper end, as shown in the figure

Water, in consequence of its extensive power of dissolving bodies of various kinds, is not met with naturally in a state of perfect purity. *Rain water*, collected in the open country after continued wet weather, is nearly pure, but even this contains the gases of the atmosphere dissolved in it, usually to the extent of from about 30 to 50 c c in a litre of water, besides particles of solid suspended matters

The presence of air in water is necessary to the life of fishes and aquatic animals generally, for it is by means of the oxygen thus dissolved that they maintain respiration. Its presence may be shown as follows —

Fig 12



Exp 35.—Fit a quill tube, *a* (Fig 12), by means of a sound cork to a Florence flask, having first filled the flask with rain water, or with spring water, fill the tube also completely with water, and adapt it to a small glass jar, *b*, also filled with water, and standing in the water-bath. Heat the water in the flask till it

boils briskly; bubbles of air will gradually be driven out of the water, and may be collected in the glass receiver, *b*.

Rain water which falls in mountainous or rocky districts formed of millstone grit, mica slate, and other rocks which contain but little soluble material, generally runs off nearly free from anything except a little vegetable matter and dissolved gases; but *spring water*, although it may be perfectly colourless and transparent, contains some salts in solution. The quantity and the kind of these salts varies with the kind of rock or soil in which the spring originates.

The salts most often found in spring water are sodic chloride or common salt, calcic carbonate from chalk, and calcic sulphate, as well as small amounts of magnesian carbonate and sulphate. The waters of town wells also generally contain traces of ammonia, and more or less of the nitrates and nitrites of calcium or of sodium. The nitric acid in these salts is the result of the gradual oxidation of the drainage from animal refuse, which, though in its recent state one of the most noxious impurities that can be found in water, yet when completely oxidized into nitrates is no longer dangerous to health. Nearly all spring waters contain also a very small quantity of silica in solution. Wholesome waters do not contain in solution more than one gram of saline substances per litre; and the most highly prized sources contain but a few centigrams only in a litre of water.

Exp. 36.—Select a thin porcelain dish which will hold 60 or 80 cub. cm.; place it in one pan of the balance, and cut a piece of lead till, when placed in the other scale-pan, it counterpoises or exactly balances the dish. Measure off half a litre of spring water, and pour some of this water into the weighed dish; place it over a very small gas flame, so as to evaporate the water gently without allowing it to boil; add the rest of the water from time to time until the half litre has been completely evaporated away. Dry the salts thus obtained, and weigh what is left as accurately

as you can. By multiplying this quantity by 2 you will obtain the amount of soluble solid substances per litre which that particular specimen of water contained.

This is the basis of the plan which, with many additional precautions, is adopted for determining the quantity of salts in the process of analysing waters to be used for drinking or manufacturing purposes.

River water often holds a smaller proportion of salts dissolved in it than spring water ; and yet it may be less fit for drinking, for it generally contains a much larger quantity of organic matter ; that is to say, it contains a larger proportion of soluble drainage products of a vegetable or animal nature, which have been washed off the surface of the soil by the rain, or which have been emptied from sewers into the stream.

Such sewerage products should not be allowed to escape into rivers until they have been more or less purified by allowing the liquid to run over cultivated land, which is manured by it in its progress. The liquid afterwards runs away comparatively harmless.

Happily for mankind, running water is endowed with a considerable amount of purifying power, due to the oxygen of the air which it holds in solution. Vegetable matters consist almost entirely of carbon, oxygen, and hydrogen, with a very small proportion of nitrogen ; whilst animal matters, in addition to carbon, oxygen, and hydrogen, contain a considerable proportion of nitrogen ; both vegetable and animal matter likewise contain a little sulphur, either as sulphates or in some other form. During putrefaction these organic bodies give out a disgusting odour, and, if swallowed in this state, even when largely diluted with water, may cause serious illness. By the action of the oxygen dissolved in the water, the hydrogen of these compounds becomes changed into water, the carbon into carbonic acid, and most of the nitrogen into nitric acid. The continual motion of the water exposes fresh surfaces to the

air; fresh oxygen is in consequence always being absorbed, and the oxidation which takes place is generally sufficient to preserve the stream in a wholesome state. But if the water be overloaded with organic refuse, or if it become stagnant, the whole of the dissolved oxygen may become absorbed by the decaying matter without renewal from the air, and the pool will then emit an offensive odour, and may become a centre of disease. The filtration through the well aerated porous soil which water naturally undergoes before it issues in the form of springs, is attended with an oxidizing and purifying action of the highest importance.

River water should always be filtered through sand or through a charcoal filter before it is used for drinking. Suspended matters, such as clay, fish spawn, or small animals may be thus removed, but the salts in solution are not sensibly affected by such filtration.

Exp. 37.—Dissolve 0.395 gram of potassic permanganate in 1 litre of water, and add 3 c. c. of this solution to a mixture of 2 c. c. of dilute sulphuric acid (40 of water and 1 of acid) with half a litre of distilled water, in a glass flask, so as to give the liquid a distinct purplish tinge; little or no change of colour will be seen at the end of three hours, if the mixture be left to itself. Do the same thing with an equal quantity of river water: in three hours' time the tint will have become reddish or brownish, if any considerable quantity of organic matter be dissolved in the water.

The foregoing result may be thus explained: The sulphuric acid separates permanganic acid from the salt, and in the presence of organic matter this acid loses a portion of its oxygen, which combines with the constituents of the organic matter, while the permanganic acid becomes converted into a compound of manganese of a different and less intense colour, and containing less oxygen.

A weak solution of the permanganate, indeed, furnishes a valuable comparative test of the fitness of water for drinking. If the permanganate does not alter sensibly in

colour in such an experiment, there is no organic impurity to be feared in the water

Water is commonly spoken of as *hard* or *soft*, according to its action upon soap. Soap is a combination of a fatty or oily acid with soda, and this compound is readily soluble in pure water. Waters which contain salts of calcium or magnesium cause the soap to curdle, since these metals furnish with the fatty acid of the soap compounds which are not soluble in water. Such waters are said to be *hard*. Soap which is thus curdled is consumed in waste. In such water soap neither cleanses nor produces a lather until the whole of the earthy salts have been decomposed and an excess of soap is present. Soft waters, on the contrary, do not contain these earthy salts, and they dissolve the soap without difficulty, and without destroying either its cleansing power or its tendency to form a lather.

Many waters exhibit what is called *temporary* hardness, such waters become softer by boiling. The hardness in this case is due to the presence of calcic or magnesian carbonate. These compounds are scarcely soluble at all in pure water, but they become soluble to a considerable extent in water charged with uncombined carbonic acid. When such waters are boiled, the carbonic acid is driven off by the heat, and the calcic and magnesian carbonates which the acid had dissolved become deposited, and a 'fur' or incrustation takes place on the inside of the boiler, as may be seen by examining a kettle used for boiling such waters.

Exp 38 — Place half a litre of a water of the kind just referred to, such as that of the Thames or of the New River, in a glass flask, and boil it over a lamp for a quarter of an hour. Little crystalline grains of the earthy carbonates which were in solution will gradually be deposited, and the water will be found to be considerably softened.

Exp 39 — Mix another half litre of such a water before it is boiled with about one-eighth of its bulk of lime-water. The liquid will become turbid, and on standing for a few hours, till it is clear, it will be found to be much softer than before.

The reason of this result is, that the lime in the limewater has combined with the carbonic acid which the river water held dissolved. Chalk is thus formed, and at the same time the chalk previously dissolved by the carbonic acid becomes separated, so that both the lime of the limewater, if it be not added in too large a proportion, and that originally in the water dissolved as chalk, become precipitated* together, and the water is softened.

Exp 40—Prepare a mixture of about equal parts of strong spirit and water, so as to obtain a liquid of sp gr 0.920, and in half a litre of this dissolve 0.1 gram of curd soap. Into a glass bottle fitted with a stopper, and capable of holding about 100 c c, measure off 50 c c of such a hard water, then add, little by little, some of the spirituous solution of soap. Put the stopper into the bottle, and shake it briskly for a minute. No lather will be formed at first, but the soap will be curdled. Continue to add the solution, shaking briskly between each addition. At length there will be more soap added than the lime salts can decompose, and as soon as this happens a lather will be formed in the bottle.

This is the principle upon which Dr Clark's *soap test* for determining the hardness of water is based. In applying this test the strength of the soap solution is first carefully ascertained, and then the exact proportion necessary to produce a lather is determined for each particular water, by means of tables constructed for the purpose, the hardness of the water is then easily calculated.

Besides this temporary hardness in water, there is a *permanent* form of hardness. Indeed, very commonly the same water exhibits hardness of both kinds. The amount of each may be found by applying the soap test to the water before it has been boiled, and again after boiling it for half an hour,

* When a clear liquid becomes cloudy or milky from the addition of another clear liquid, the chemical change is attended with the formation of some insoluble compound, which is separated, or, in chemical language is *precipitated* from the liquid. The insoluble substance is called a *precipitate*, whether it sinks to the bottom or floats in the solution.

taking care to add distilled water if necessary to supply the exact quantity which has been boiled away.

The difference between the hardness of the water before it was boiled and that found afterwards gives the temporary hardness ; while the degree of hardness which remains after the boiling represents the amount of permanent hardness. This permanent hardness is due to the presence of salts of calcium or magnesium other than the carbonates, such as the sulphates or nitrates.

Waters having this permanent kind of hardness may be softened by a method well known in the laundry ; for by the addition of sodic carbonate, or common washing soda, the calcium or magnesium is precipitated as carbonate, while sodic sulphate or nitrate remains dissolved. For instance, with calcic sulphate the change may be thus represented :



The sodic sulphate which is formed does not curdle the soap.

Mineral waters hold a much larger quantity of substances in solution than waters used for domestic purposes. If such waters contain iron, they have an inky taste, like some of those at Tunbridge Wells. They are called *chalybeate* waters, and may be known by the rusty deposit which they form when exposed to the air. Others are strongly *effervescent*, like seltzer water, owing to the escape of carbonic acid ; while others have a strong *sulphuretted odour*, like the Harrogate water, owing to the presence of sulphuretted hydrogen. Others, again, are strongly *saline*, like the springs at Epsom and at Cheltenham ; whilst in some cases in volcanic districts, as in the Geysers of Iceland, the water is actually boiling hot, and holds silica dissolved ; and in the Bath waters the springs, though not boiling, are much hotter than the surface of the soil from which they come forth, owing to the action of subterraneous heat.

Sea water is largely loaded with common salt, and with magnesian chloride and sulphate, to which last the bitter taste is due. It contains also a large number of other salts; among these are small proportions of bromides and iodides. A litre of sea water contains about 37·5 grams of various salts dissolved in it; about 29 grams of these consist of sodic chloride.

Water dissolves certain bodies, such as common salt, nitre, and Epsom salt, with great ease; but other salts, such as calcic sulphate, are soluble in much smaller proportion in the same quantity of water. When water has dissolved as large a proportion of any substance as it can take up, it is said to be *saturated* with that substance. Some substances, such as silver chloride and siliceous sand, are not soluble in water to any sensible extent. Generally speaking, water, though saturated with any particular salt when cold, will dissolve a larger quantity of the same salt when heated.

Exp. 41.—Grind up in a mortar 50 or 60 grams of sodic sulphate with about twice its weight of water at 15° C. The water will dissolve a considerable proportion, but not the whole of the salt. Pour this saturated solution into a flask, and warm it gently; it will now dissolve 50 grams more of the salt without difficulty. Allow the solution to cool down to the temperature of the air, say 15° C. : long four-sided needles will crystallise from the liquid. Pour off the liquid, and dry the crystals by pressing them between a few folds of blotting-paper. When they appear to be dry, put a small quantity of the crystals into a test-tube, and apply a gentle heat : the salt will liquefy, and on continuing to apply the heat a large quantity of water will be driven off, and a dry white powder will be left in the tube.

The water thus given off was chemically combined with the crystals. Many other salts which appear to be perfectly dry to the touch, give off water when heated, and crumble down to a shapeless mass; such, for example, as alum, cupric sulphate and sodic carbonate; but they all lose the dis-

tinative form of their crystals when the water has been expelled. If the dry residue be again dissolved in water, new crystals similar to the original ones are obtained, and they are found also to contain water as before. The quantity of water is definite for each salt; for instance, sodic sulphate contains 10 atoms of water combined with each atom of the salt, and its composition is represented by the formula $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$; cupric sulphate has 5 atoms ($\text{CuSO}_4, 5\text{H}_2\text{O}$), sodic carbonate 10 atoms to each atom of the salt ($\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$), and so on. Such water which is necessary to the form of the salt, but which can be driven off without altering its chemical character, is called *water of crystallisation*. Sometimes mere exposure of the salt to the air is sufficient to get rid of this water of crystallisation.

Exp. 42.—Take some of the fresh crystals of sodic sulphate; let them lie exposed on a piece of blotting-paper for two or three days. They will gradually lose their water, and crumble down, or *effloresce* into a white powder.

Other salts act in the opposite manner. They absorb moisture from the air, and become dissolved in it: they *deliquesce*.

Exp. 43.—Put a little calcic chloride in a watch-glass, and expose it to the air; do the same with a few decigrams of potassic carbonate; in two or three days both salts will be found in a liquid state.

The compounds of water are often called *hydrates* (from the Greek *ὕδωρ*, water); and when a substance is entirely free from water in combination, it is said to be *anhydrous*. When a salt is dissolved in water, it is not considered by the act of solution to have entered into true chemical combination; the water and the salt may be separated from each other unchanged by merely altering the temperature a few degrees. Many other substances besides water dissolve bodies without acting chemically on them. Spirit of wine

dissolves camphor, coal naphtha dissolves caoutchouc, and each is left unchanged when the spirit or the naphtha evaporates.

In a case of true chemical action, the result is different; the product obtained differs in properties from the original bodies. When potassium is thrown into water, the metal disappears, and seems to dissolve, but it cannot be removed by evaporation. The water has been decomposed, hydrogen escapes, and on evaporation a solid compound of potassium and hydrogen with oxygen, in perfectly definite proportions, is obtained (KHO), and this may be made red hot without being chemically altered.

(16) HYDROGEN: *Symb.* H; *Atomic Wt.* 1; *Atomic Vol.* \square ; *Mol. Wt.* H_2 , 2; *Mol. Vol.* \square ; *Sp. Gr.* 0.0691; *Rel. Wt.* 1.

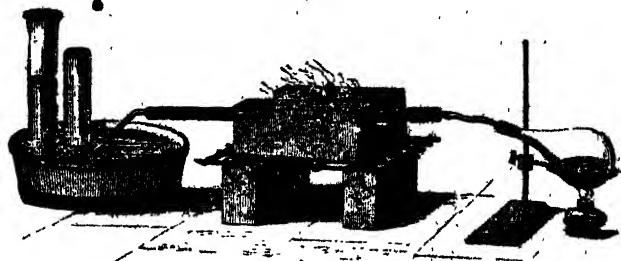
We have already found that when sodium or potassium is placed in water an immediate escape of hydrogen occurs, as a colourless inflammable gas.

Potassium and sodium are among the few bodies which act powerfully upon water at common temperatures: there are some other metals which when cold, have scarcely any action upon it, though when made red hot they easily decompose it. Iron is one of these metals.

Exp. 44.—Procure an iron gaspipe about 60 centim. long and 2 centim. in diameter; fit a cork and a short piece of glass tube to each end. Introduce some iron filings into the iron tube. To one end attach a quill tube by means of a flexible caoutchouc tubing; and to the other, also by means of a vulcanised rubber tube, fasten a Florence flask about one-third full of water, fitted with a cork and quill tube. Make a temporary furnace (as shown in Fig. 13) by means of six or eight bricks, with a grating, which may consist simply of a coarse piece of wire gauze; support the iron tube across the furnace, and make it red hot by surrounding it with burning charcoal. Then cause the water in the flask to boil with such force as to drive the steam

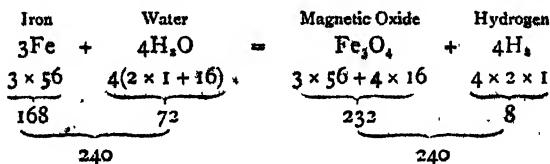
through the red-hot pipe over the heated iron filings. Gas will come off at the other end, and may be collected in jars over the

Fig. 13.



pneumatic trough. When a light is applied to it, it will burn with a pale yellowish flame. It is, in fact, hydrogen.

In this process the red-hot iron has removed the oxygen from the vapour of water, and left the hydrogen in a separate form, magnetic oxide of iron being produced. The decomposition may be thus represented :



The usual and the most convenient mode of preparing hydrogen is the following :—

Exp. 45.—Melt about half a kilogram of zinc in an iron ladle, and pour it in a thin stream from a height of about a metre into a pailful of cold water ; the metal will be obtained in flakes, and is said to be *granulated*. Introduce into a bottle which will hold about 300 c. c. about 15 grams of granulated zinc ; fit a good cork to the neck of the bottle ; then remove the cork and pierce two holes in it with a round file ; through one hole pass a glass tube funnel, and through the other a tube bent as in Fig. 14. To the bent tube attach another bent glass tube, by means of a

Formation of Hydrogen.

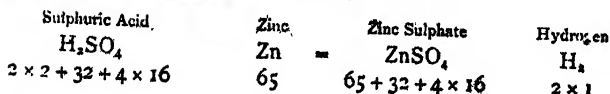
piece of vulcanised rubber tubing. Next pour upon the zinc through the funnel about 70 c. c. of diluted sulphuric acid (1 measure of strong acid to 7 measures of

Fig. 14.



water). A brisk effervescence will occur, and a colourless gas will come off, which may easily be collected in jars over the pneumatic trough.

In this case the zinc appears to displace hydrogen from the acid; a new salt (zinc sulphate) is formed, and becomes dissolved in the water. The reaction is shown in the following equation:—



Scraps of iron may be used instead of zinc in this experiment; but the gas then has a disagreeable smell, owing to the presence of carburetted hydrogen derived from the carbon in the iron. Ferrous sulphate (FeSO_4) is now formed instead of zinc sulphate.

Hydrogen is not a poison when breathed, but it cannot support life. It is very slightly soluble in water; 100 c. c. of water dissolve only 1.93 c. c. of the gas.

Hydrogen is a colourless gas; when pure it is without either taste or odour. It has never been liquefied by cold or pressure. Owing to its lightness it was at one time used for filling balloons; but coal gas is now substituted for it, as, though not so light as hydrogen, it is more easily obtained in sufficient quantity.

Exp. 46.—Hold a small jar, with its mouth downwards, over the tube of the hydrogen bottle while it is giving off gas freely, as shown in Fig. 15. The hydrogen will gradually displace the heavier air, and may be found in the jar even after the lapse of two or three minutes, if the mouth of the jar be kept downwards,

as may be proved by applying a flame, when it will take fire; but if the mouth be turned upwards, the gas will escape in a few seconds, and no flash will occur on applying a light.

Hydrogen in burning gives out little light, but much heat; a jet of the gas burns with a pale yellowish flame.

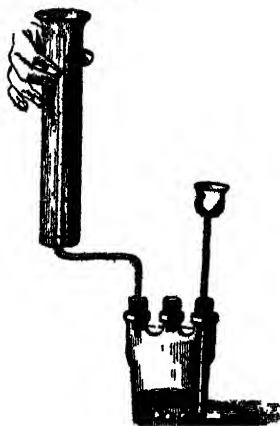
All gases which are formed in contact with water necessarily contain a certain small amount of moisture in the invisible form; but they may be freed from this when necessary by causing the gas to pass slowly over some salt, which, like calcic chloride, has a strong attraction for moisture.

For the purpose of removing this small quantity of moisture from hydrogen, as ordinarily prepared, the following arrangement may be made:—

Exp. 47.—Fill a tube of about 20 centim. long with calcic chloride broken into pieces about the size of a pea; plug each end loosely with cotton wool; then fit a cork, pierced with a quill tube 5 centim. long, into each end; fasten this drying apparatus to the hydrogen bottle by means of the caoutchouc tube. The gas as it comes out at the other end of the drying tube will be dry. Now set fire to the dry gas as it escapes, and hold a cold glass jar over the burning jet. The side of the glass will quickly become bedewed with moisture, owing to the union of the burning hydrogen with oxygen obtained from the atmosphere.

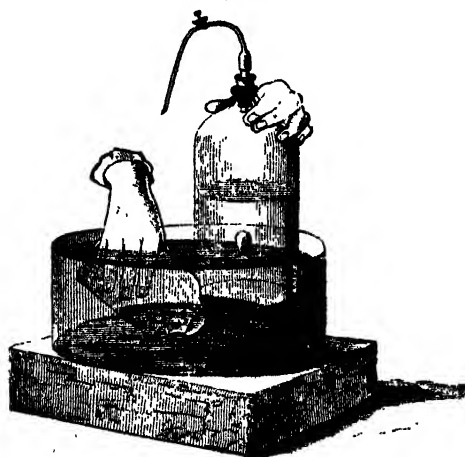
Oxygen and hydrogen may be kept mixed together at ordinary temperatures for any length of time without combining; but if an electric spark be applied to the mixture, or a lighted or even a glowing match, immediate combination occurs, with a bright flash and a loud report.

Fig. 15.



Exp. 48.—Fit a good cork into the neck of a gas jar, and pass a quill tube 5 centim. long through it. Bind a short piece of caoutchouc tube firmly to the quill tube, and close this elastic tube with a small screw vice or tap made for such purposes. Fill the jar with water over the pneumatic trough. Now fill a small jar which will hold about half a litre with oxygen, and transfer it by manipulating, as shown in Fig. 16, without loss to the gas jar. Fill the same jar with hydrogen, and transfer it to the large jar. Repeat the operation with the hydrogen, so as to obtain in the larger jar a mixture of half a litre of oxygen

Fig. 16.



and 1 litre of hydrogen. Having previously softened a thin bladder by soaking it in water, tie into the neck of it a glass quill tube 5 centim. long: then adjust to the projecting portion a piece of vulcanised caoutchouc tubing provided with another screw tap. Press the air out of the bladder; connect by means of a short piece of glass tubing the two pieces of vulcanised tube; depress the jar in the pneumatic trough, and then open each screw tap. The gas will now pass into the bladder; close both screw taps, and remove the bladder. Now place the end of the tube attached to the bladder under some soapsuds, and

force out the mixed gas by squeezing the bladder so as to make a lather. Carefully remove the bladder to a distance, and then apply a light to the froth of soapsuds. A loud explosion will immediately follow.

In this experiment steam is formed; this first expands considerably, owing to the heat produced by the combination of the oxygen and hydrogen, and immediately afterwards the steam becomes condensed, the particles of the surrounding air rush in to fill the void, and by striking one against the other produce the report.

If the hydrogen be mixed with air, instead of pure oxygen, a similar but weaker explosion occurs when a light is applied. In all experiments with hydrogen it is therefore necessary to allow time for the expulsion of the air from the apparatus before setting fire to the gas as it comes out. If the mixture be diluted with a large excess of hydrogen or of air, the explosion becomes less sudden, and less heat is given out; until, when the dilution reaches a certain point, the mixture only burns quickly without explosion, and, if still more diluted, the combustion only takes place at the spot where heat is applied.

The proportion of oxygen and hydrogen which unite together is perfectly defined, no matter in what proportion they are mixed. One measure of oxygen invariably unites with exactly two measures of hydrogen. If the gases before firing are heated beyond the temperature of boiling water, and be kept at the same temperature after the explosion,* the three measures of gas which have united will form exactly two measures of steam—

It might be considered that we now have proved the true composition of water, for we have found that water may by analysis be made to yield both oxygen and hydrogen, and

* This form of the experiment requires special apparatus, and, except in practised hands, is rather difficult of performance

that when oxygen and hydrogen are burned water is formed ; but at present we have not shown absolutely that oxygen and

hydrogen are the only substances which enter into the formation of water.

The following mode of experiment, for which a somewhat costly form of apparatus is required, proves this fact, however, in a conclusive manner.

Exp. 49. — Fig. 17 represents a strong glass vessel A, through the upper part of which two platinum wires are inserted; the vessel can be closed by a glass stop-cock C; by means of a second stop-cock it can be attached to an air-pump, not shown in the figure, and the air exhausted.

The stop-cocks having been

closed, the vessel is screwed upon the top of a jar, B, containing a mixture of two measures of hydrogen and one measure of oxygen. On opening the stop-cocks a portion of the mixture enters the vessel; the cocks are then closed, and an electric spark passed through the mixture. A bright flash occurs; the gases combine, and the whole of the two gases become condensed into water, which trickles down the sides of the glass. On again opening the stop-cocks a fresh quantity of gases may be admitted, to supply the place of those just condensed. The spark may be again transmitted, and the process may be repeated until the whole of the gases are consumed and a considerable quantity of water formed.

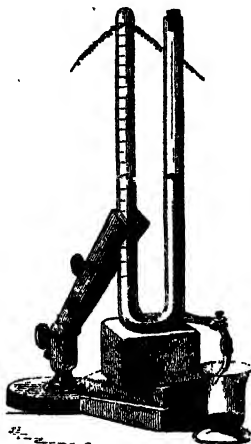
If in this experiment oxygen or hydrogen be used in excess, that excess will be found in the vessel unacted on after firing the mixture.

Fig. 17.



Exp. 50.—Provide a stout tube bent into the form shown in Fig. 18, open at one end and sealed at the other, the sealed limb having been divided into cubic centimetres, or other equal divisions. Into the sides of the tube, near the sealed extremity, two platinum wires are fused, with two of the ends inside the tube, nearly touching each other. Fill the tube with mercury; then introduce a mixture of 4 volumes of oxygen and 2 volumes of hydrogen. The bulk of this gas is to be carefully measured; say it fills 6 divisions after causing the liquid metal to stand at the same level in both tubes; this may be easily effected either by adding mercury or by drawing it off through the caoutchouc tube and screw-tap near the bottom. The open end of the tube must now be firmly closed with a cork, below which a column of air is included. This air is meant to act as a spring for gradually checking the force of the explosion, which is now to be produced by passing an electric spark either from a Leyden jar or an induction coil between the wires. After the explosion the gas in the closed limb will measure less than before. With-

Fig. 18.



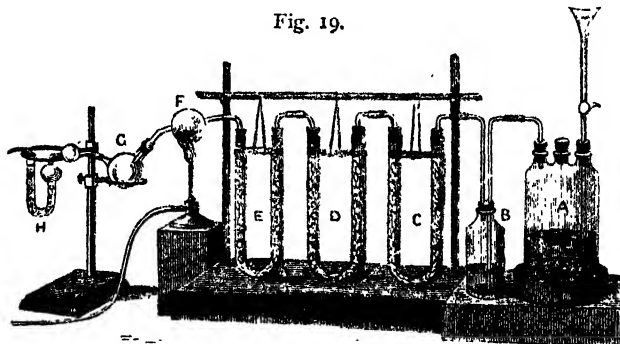
draw the cork, and add mercury until the metal again stands at the same height in both tubes. Suppose the gas filled 6 divisions before the spark was passed; it fills just 3 divisions afterwards: the 2 volumes of hydrogen which the mixture contained combine with 1 volume of oxygen, and immediately condense into moisture on the cold sides of the tube. The remaining 3 volumes may be shown to be oxygen as follows:—Fill up the open limb with mercury; close it with the thumb; then incline the tube so as to transfer the gas from the sealed to the open limb. A match with a red-hot point will immediately blaze up if introduced into it (*Exp.* 7).

Such an instrument (Fig. 18) is called a *eudiometer*, and is often used for the analysis of mixtures of gases.

Pure water may also be formed in considerable quantities by the following method, which rests on this important fact, that when cupric oxide is heated in contact with hydrogen, it gives up its oxygen to the hydrogen, and the two unite to form water, which may not only be collected and weighed, but the proportion by weight of each of its constituents may also be determined.

Exp. 51.—Place a quantity of pure and dry cupric oxide (CuO) in a globe, *F* (Fig. 19), made of glass of difficult fusibility, and weigh the globe and its contents accurately. Hydrogen is next to be disengaged steadily, by adding small quantities of

Fig. 19.



diluted sulphuric acid to granulated zinc contained in the bottle *A*. Let the gas bubble up through a solution of potash in *B*, and then pass through the tube *C*, which is filled with fragments of pumice moistened with a solution of corrosive sublimate (HgCl_2), then through *D*, which is filled with pieces of fused potash, and lastly through *E*, which contains fragments of pumice moistened with strong sulphuric acid. The potash and the mercuric salt remove traces of arsenicum, sulphur, and carburetted compounds derived from impurities in the acid or the zinc, while the tube *E* deprives the gas of every trace of moisture. In this way pure and dry hydrogen is obtained before it passes into the globe *F*. When all the air of the apparatus has been displaced, by allowing a certain quantity of hydrogen to pass through it to waste,

heat is applied to the globe F. The cupric oxide when heated alone is not altered, but when heated with hydrogen it loses oxygen, which converts the hydrogen into water; this is collected in the receiver G and the bent tube H, which contains pieces of pumice moistened with strong sulphuric acid. When the globe F is cold, pass a current of air through the apparatus, for the purpose of displacing the hydrogen left in it. Weigh the globe with the oxide a second time: the loss shows how much oxygen has been removed. Weigh also the receivers G and H, again: the increase in weight shows how much water has been condensed; the difference between the oxygen lost by F and the water gained by G and H is the hydrogen which has combined with the oxygen to form water.

By numerous careful experiments performed in this way it has been found that 16 grams of oxygen combine with exactly 2 grams of hydrogen to form 18 grams of water.

Hydrogen, in combining with oxygen, gives out a heat surpassing that which any other chemical action produces. By forcing a jet of oxygen through the flame of a spirit lamp, of coal gas, or of hydrogen, a very high temperature is immediately obtained; but the most intense heat is procured by sending a jet of oxygen into the midst of a jet of hydrogen by means of two concentric tubes, as shown in Fig. 20.* The outer tube, provided with the stop-cock H, is connected with a large bladder or bag of hydrogen, placed under a weighted board, which by its pressure drives out the gas, while the inner tube, with its stop-cock O, is connected with another bag, which supplies oxygen. If the mixed gas, as it issues, is kindled, a small feebly luminous but intensely hot jet of

Fig. 20



flame is obtained, in which a thick platinum wire may be quickly melted and partially volatilised. Thick iron and steel wires held in this flame are also easily melted, and burn, giving off brilliant sparks. Rock crystal melts in it like glass, and the stem of a tobacco pipe fuses without difficulty. If the jet be directed on a pellet of lime, the earth does not fuse, but becomes white hot, giving out a very pure white light, which, under the name of the 'Drummond light,' has been extensively used for signalling, and, when properly mounted in the focus of a concave mirror, has been seen, from great elevations, at a distance of more than 100 miles.

The combustion of the *mixed* gases, as the oxygen and hydrogen in proper proportions are termed, produces, as we know, pure water. Water is also formed abundantly whenever combustible bodies which contain much hydrogen are burned in the open air; such, for instance, as wood, oil, tallow, spirit of wine, and coal gas. A tallow candle, in burning, produces rather more than its own weight of water; and alcohol or spirit of wine yields a still larger amount.

Exp. 52.—Hold a cold glass over a burning candle: it will quickly become bedewed with moisture.

A similar result may be observed every time a retort or vessel containing cold liquid is heated over the flame of a lamp or of gas: drops of water condense until the vessel becomes sufficiently hot to prevent this effect from occurring.

Hydrogen is rapidly absorbed by many porous bodies, particularly by the metals platinum and palladium. Palladium, indeed, can absorb as much as 900 times its bulk of hydrogen gas without losing its brilliant lustre. It retains the gas at ordinary temperatures, but loses it by degrees if the temperature be raised; and if heated to redness, in a vessel from which the air is exhausted, all the hydrogen may be again extracted.

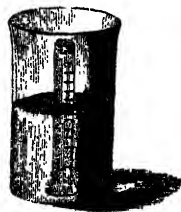
Exp. 53.—Fasten a piece of *spongy* platinum (a form in which the metal may be obtained by heating its compound chloride [$2\text{H}_2\text{NCl}$, PtCl_4], as will be explained hereafter) to a thin platinum wire, and hold it in a jet of hydrogen as it escapes into the air. The cold platinum will become red hot, and kindle the gas.

This effect appears to be due to the condensation of the gas by the platinum, which also condenses oxygen from the air, and the heat attending the condensation is sufficient ultimately to set fire to the mixture of gases.

Another peculiar property of gases is well exhibited by hydrogen. Whenever two gases are placed in vessels which communicate with each other, the gases become gradually intermingled, although they may not have any tendency to chemical combination; and the greater the difference in density between them, the more rapidly does this process of *diffusion*, as it is called, take place.

Exp. 54.—Take a tube of about 20 centim. long and 2 centim. wide, open at both ends. Mix a little plaster of Paris with water so as to be of the consistence of thick cream, and immerse one end of the glass tube in the mixture to the depth of 5 mm. In about ten minutes the plaster will have become solid, and on raising the tube out of the mixture its extremity will be closed with a thin plate of plaster; let it dry in a warm room for a couple of days. Through this porous plug the effects of diffusion may be observed. Fill this *diffusion-tube* with hydrogen gas by displacement,* covering the plug of plaster with a cap of tinfoil when the tube is full of hydrogen. Place it in a tall jar of water (Fig. 21), with the open end downwards, and remove the tinfoil. The water will rise rapidly in the tube, as though it were dissolving the gas, and will soon fill it above two-thirds of its height.

Fig. 21.



In this experiment the porous plug favours the diffusion of the hydrogen: about 3·8 measures of hydrogen pass out, while only 1 measure of air enters; hence the liquid rises in the tube. (*See Appendix.*)

Other gases exhibit a similar tendency to diffusion, though to a less extent, the diffusiveness depending upon the relative density of the two. Its amount admits of exact calculation, supposing the specific gravity of the gas to be known. The rule is to take the square root of the number which represents the specific gravity of the gas, and divide 1 by this number: the fraction thus obtained is the diffusiveness required.

For example, the numbers which represent the specific gravity of oxygen and hydrogen, 1.1057 and 0.0691, are to each other in the proportion of 16 to 1. The square root of 16 is 4, and the square root of 1 is 1. Now, the rate at which hydrogen diffuses into an atmosphere consisting of pure oxygen is as 4 to 1. That is to say, that when proper precaution is used in making the experiment with such a diffusion-tube as that described, while 4 measures of hydrogen pass out into the oxygen through the plaster, 1 measure of oxygen would pass into the hydrogen in the opposite direction. The specific gravities of air and hydrogen are

1 and 0.0691, and their rates of diffusion are $\frac{1}{\sqrt{1}} (= 1)$ and $\frac{1}{\sqrt{0.0691}}$, or 1 and 3.8. In fact, 3.8 measures of hydrogen become diffused into the air, while 1 measure of air is being diffused at the same time into the hydrogen.

Hydrogen is the lightest substance known; an equal bulk of oxygen being 16 times as heavy, and an equal bulk of air 14.47 times as heavy as the same bulk of hydrogen under similar circumstances of temperature and pressure. Hydrogen has also a smaller combining number than any other elementary body; and this, with its lightness, furnish two of the reasons which have induced chemists to take hydrogen as the *unit* or standard of comparison both for atomic weights and combining volumes. The atomic weight of hydrogen has been therefore taken as 1, or $H = 1$, and its combining volume is also 1, or $H = \square$.

Suppose, then, 1 gram of hydrogen to be the unit of weight, the space it would occupy at 0° , under a barometric pressure of 760 mm., would be 11.19 litres. The same volume of oxygen would weigh 16 grams, of nitrogen 14 grams, of chlorine 35.5 grams. This volume, 11.19 litres, may, therefore, be regarded as representing 1 gas volume. For many purposes, however, the litre is a convenient measure; and 1 litre of hydrogen, at the temperature of 0° and 760 mm. pressure, weighs .896 milligrams.



The proportion in volume in which a certain fixed volume of each of the elementary gases or vapours combines with hydrogen, and the volume of gas or vapour which such combinations furnish, compared with the space they occupy before combination, affords a character upon which the grouping of the different elements into natural families is founded.

For example, when a litre of chlorine unites with hydrogen, it does so in the proportion of 1 litre of hydrogen, and it forms with it 2 litres of a new compound, hydrochloric acid gas; but a litre of oxygen, when it unites with hydrogen, requires not less than 2 litres of hydrogen, though it still forms only 2 litres of the new body, aqueous vapour; further, if a litre of nitrogen be combined with hydrogen, it will unite with 3 litres of hydrogen, and yet will form only 2 litres of the resulting ammoniacal gas. Consequently, if the hydrochloric acid be represented by the symbols HCl , it is agreed by chemists to represent the equal bulk of aqueous vapour as H_2O , and the same bulk of ammonia as H_3N .

We see, then, that a single volume of chlorine, of oxygen, and of nitrogen, when uniting severally with hydrogen, requires, respectively, one, two, and three volumes of hydrogen, while in every one of these cases the compound which is formed measures two volumes, no matter whether the volume used be a cubic centimetre, a litre, a cubic inch, a cubic foot, or any other volume which may be agreed on.

Further, it is important to remember that the quantity of

any compound represented by its formula is spoken of as its *molecule*; and when the body is known in the aeriform state, that molecule is always tacitly compared with an equal bulk of hydrogen, which is represented by the formula H_2 ; and this amount of hydrogen is also spoken of as its molecule.*

In the table which follows, some of the most important gaseous compounds of the different elements are enumerated. In each case the quantity represented by the formula indicates 2 volumes, say 2 litres, of the gaseous compound. $H = 1$, being  1 volume or 1 litre, and $H_2 = 2$ volumes  or 2 litres.

In the first column all the compounds are represented in their formulæ as furnished by the union of single volumes of each element, the two bodies combining volume to volume. Elements which combine in this way are called *monads*, or *univalent* elements.

In the second column two volumes of hydrogen are represented in combination with a single volume of certain other elements, which, from their power of chemically uniting with two volumes of hydrogen, have been termed *dyads*, or *bivalent* elements.

In the third column each of the compounds contains 3 volumes of hydrogen united with 1 volume of one of the elements of a natural group known as the *triads*, or, as they are sometimes called, *trivalent* elements,† 1 volume of each of these element requiring 3 volumes of hydrogen to form the compound.

And, lastly, in the fourth column the compounds represented each contains 4 volumes of hydrogen, united with a fixed quantity of certain elements, which cannot be obtained

* Some further observations on gaseous molecules will be found in the paragraph on the atomic theory.

† Phosphorus and arsenicum are, however, exceptional, since they combine with 3 volumes of hydrogen in the proportion of $\frac{1}{2}$ a volume of their vapour.

separately as gases, but which are distinguished as *tetrads*, or *quadrivalent* elements.*

COMPOUNDS OF MONADS	COMPOUNDS OF DYADS	COMPOUNDS OF TRIADS	COMPOUNDS OF TETRADES
Hydrochloric Acid HCl	Water H ₂ O	Ammonia H ₃ N	Marsh Gas H ₄ C
Hydrobromic Acid HBr	Sulphuretted Hydrogen H ₂ S	Phosphuretted Hydrogen H ₃ P	Siliciuretted Hydrogen H ₄ Si
Hydriodic Acid HI	Seleniuretted Hydrogen H ₂ Se	Arseniuretted Hydrogen H ₃ As	
Hydrofluoric Acid HF	Telluretted Hydrogen H ₂ Te	Antimoniuretted Hydrogen H ₃ Sb	

The compounds which hydrogen forms when it unites with any other elementary body are known as *hydrides*.

CHAPTER IV.

OXIDES OF CARBON—CARBON.

(17) CARBONIC ANHYDRIDE (*Carbon Dioxide*, or *Carbonic Acid*): Symbol, CO₂; Atomic Weight, 44; Atomic and Molecular Volume, ; Specific Gravity, 1.529; Relative Weight, 22.

We have already seen that when a saucer containing limewater is exposed to the air for a few minutes, the surface of the limewater becomes covered with a thin insoluble crust

* The elements which combine with 1, with 3, or with an uneven number of volumes of hydrogen are sometimes further distinguished as *perissad* elements; and those which combine with 2, 4, or an even number of volumes of hydrogen are called *artiad* elements.

or pellicle, consisting of chalk, which is formed by the union of carbonic anhydride contained in the atmosphere with the lime, $\text{CO}_2 + \text{CaO}$ forming CaCO_3 . Such compounds of carbonic anhydride with bases are called *carbonates*; hence chalk is called calcic carbonate, or often carbonate of lime. When chalk is heated to bright redness, the carbonic anhydride is driven off, and the lime is left behind, as in the ordinary process of burning limestone into lime, CaCO_3 becoming separated into CaO and CO_2 .

The carbonic is a very weak acid, and may be displaced from its compounds by almost every acid which is soluble in water.

Exp. 55.—In a glass bottle, similar to that used for preparing hydrogen (Fig. 14), place 15 or 20 grams of chalk in small lumps, or of marble, which is a crystalline form of the same chemical compound. Pour on it some strong acid, such as the hydrochloric (muriatic), HCl , diluted with 8 or 10 times its bulk of water.

In this experiment the acid exchanges its hydrogen for the calcium, producing calcic chloride (CaCl_2) on the one hand, and carbonic acid (H_2CO_3) on the other. But the carbonic acid is so unstable that it immediately becomes decomposed into water, which remains behind, and into carbonic anhydride,* which comes off as a gas with brisk effervescence. The decomposition may be represented as follows:—



Limestone (CaCO_3), pearlash (K_2CO_3), sodic carbonate (Na_2CO_3), and indeed all the carbonates, may be made to

* An *anhydride* is an oxide which, when dissolved in water, furnishes an acid, by uniting with the elements of water; and it must be distinguished from a true acid, which is always a salt of hydrogen. Some writers are not sufficiently careful to distinguish the two classes of bodies from each other. The gas CO_2 was formerly known as carbonic acid; but as it is not a salt of hydrogen, it has been found necessary to change its name for the sake of precision, and it is now called carbonic anhydride, and sometimes carbon dioxide.

furnish carbonic anhydride as easily as marble, when treated with a strong acid.

Although carbonic anhydride is usually obtained as a heavy transparent gas, without colour, and with a faintly acidulous taste and smell, it can be procured as a colourless transparent liquid, by generating it from materials packed into a small space in a strong closed tube; but it requires a pressure of 40 or 50 atmospheres to effect this; and it is not an experiment that can be made with safety by an inexperienced person. The gas is sometimes liquefied in large quantities for experimental purposes in strong wrought-iron vessels constructed with this object. When a stream of the liquid thus obtained is allowed to escape into the air, one portion of the liquid evaporates so rapidly as to carry off heat so quickly that it freezes the rest into a snow-white solid. If this be collected and mixed with ether, it produces a cold bath or freezing mixture of great intensity, owing to the rapid evaporation of the frozen gas, which carries off heat in large quantity from any substance nearest to it; a cold estimated at -75° is thus easily attained.

Exp. 56.—Fill three or four small jars with the gas as obtained in *Exp. 55*. Plunge a lighted candle into one of them: the flame is extinguished, but the gas does not take fire.

It will be remembered that other gases, such as nitrogen, put out the light.

Exp. 57.—Into another jar of the gas pour two or three table-spoonfuls of limewater. It will at once become milky, owing to the formation of chalk; two or three drops of any strong acid will immediately redissolve the chalk.

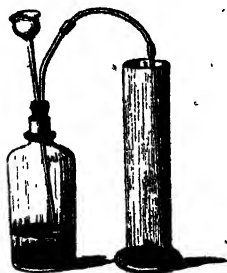
This action of the gas upon limewater is a very convenient and characteristic test of its presence, even when it is mixed largely with air or other gases, since these gases do not render limewater turbid.

Undiluted carbonic anhydride cannot be breathed, because the glottis, or valve at the entrance of the windpipe, closes and prevents it from entering the lungs; but if the

gas be largely mixed with air; that is, if it be present in a quantity varying from 3 to 4 per cent. of the respired air, it acts as a stupefying or narcotic poison, by preventing the proper action of the air upon the blood as it passes through the lungs, and in this way produces death. Part of the bad effect experienced after remaining in crowded and ill-ventilated rooms is owing to the presence of unusual quantities of this gas, the true prevention in such cases being efficient ventilation.

Carbonic anhydride is more than half as heavy again as air. It is just 22 times as heavy as hydrogen, so that 11.19 litres, at 0° C. and 760 mm. bar., weigh 22 grams, while the same volume of air weighs only 14.47.

Fig. 22.



Exp. 58.—Allow the gas to pass to the bottom of a small jar, arranged as in Fig. 22; when full, the gas, though invisible, may be shown to be there, as it will extinguish a candle lowered into it on a wire.

Exp. 59.—Take a second similar jar full of air, and pour the gas slowly into it from the jar filled as in *Exp. 58*, as though it were water. The light will now be extinguished if lowered into the second jar, but will burn if introduced into the first.

Many amusing experiments may be made upon this gas, owing to the ease with which, from its density, it may be transferred from vessel to vessel. It may be drawn off with a syphon, ladled out with a glass, and so on.

Water dissolves about its own bulk of carbonic anhydride, forming a solution of carbonic acid, $\text{CO}_2 + \text{H}_2\text{O}$ becoming H_2CO_3 . The water may be made to dissolve considerably more than its own bulk of the gas, if it be forced in under pressure. It is in this way that the so-called *soda water* is made, though the water seldom contains soda, or indeed

anything but the dissolved gas. As soon as the pressure is removed, the gas escapes with effervescence.

Exp. 60.—Cause a stream of the gas to bubble briskly through 60 or 100 c. c. of water. To a portion of the solution of the gas thus obtained add a few drops of tincture of litmus : it will be reddened. Now boil the red liquid for a few minutes : the gas will be driven off again, and the litmus will recover its blue colour.

The solution of carbonic acid exerts slight but important solvent powers upon many rocks and minerals. This action produces changes which, insignificant as the amount may appear at any given moment, yet in the lapse of ages becomes very considerable, since few natural waters are found which are not charged more or less extensively with carbonic acid.

Carbonic anhydride is largely produced in a variety of important natural operations. Respiration, or the process of breathing, both in man and animals, is always attended with the formation of a large quantity of the gas.

Exp. 61.—By means of a tube open at both ends blow a little air from the lungs through limewater ; it will speedily become turbid, owing to the formation of calcic carbonate.

Air which has been breathed once contains from $3\frac{1}{2}$ to 4 per cent. of the gas.

Exp. 62.—Pass a little of the air from the lungs, by means of a tube, into a gas jar filled with water, and standing over water. When the water has been displaced by the exhaled air, it may be tried with a lighted candle, which will quickly go out.

Fermentation is another source of carbonic acid.

Exp. 63.—Dissolve 15 or 20 grams of sugar in ten times its weight of water, at 25° C. Add two teaspoonfuls of brewers' yeast, and introduce the mixture into a Florence flask provided with a cork and bent tube for the escape of gas. In about an hour's time it will begin to give off a gas which puts out a light and makes limewater turbid.

The briskness of bottled beer and of champagne is due to

the dissolved carbonic acid which they contain. Accidents have often happened in breweries where fermentation is carried on upon a large scale, owing to the incautious entrance of the workmen into an empty fermenting vat before the heavy gas has had time to escape. The plug at the bottom should be left open after the liquor has run off, to assist the escape.

Large quantities of carbonic anhydride are also expelled in the process of burning limestone in a limekiln; and a similar action occurs if limestone is found in volcanic districts, owing to the action upon it of the heat beneath the surface of the earth, in consequence of which immense volumes of the gas escape from craters and fissures of the soil. The springs of such districts are often lightly charged with carbonic acid, and the gas passes off with effervescence when the water comes to the surface.

Much of the carbonic acid found in ordinary spring and river water is furnished by the gradual oxidation, in the pores of the soil, of the vegetable and other organic matter with which they had been before contaminated.

What is called *choke damp* by miners is also principally composed of this gas. It often accumulates in old pits or wells, and in the abandoned workings of mines. No one ought ever to venture into such places without first trying whether a candle will burn freely in the pit or shaft. If it does it is safe, at least for a short time.

Whenever charcoal, or any substance which contains carbon, such as wood, coal, oil, or tallow, is burnt, carbonic anhydride is formed in abundance.

Exp. 64.—Kindle a piece of charcoal, and plunge it into a bottle of oxygen; it will burn brilliantly. After the combustion is over, shake some limewater with the gas which remains; the immediate precipitation of chalk shows that carbonic anhydride has been formed abundantly.

Exp. 65.—Hold a glass jar full of air for a few minutes over a piece of burning charcoal; withdraw the jar, and close the

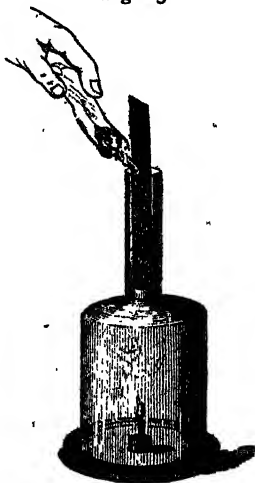
mouth of it with a glass plate. Add a tablespoonful of lime-water, and shake it up in the jar. Chalk will immediately be formed. The result will be similar if the jar be held over a jet of burning coal gas, over a burning candle, or over the flame of a spirit lamp.

Two candles of 6 to the pound, in burning, may be reckoned to produce about 38 litres of carbonic anhydride per hour, or as much of the gas as would be generated by the respiration of a man of ordinary size in the same time.

Although pure carbonic anhydride is heavier than air, both the products from a burning candle and air which has been respired are, owing to the heat produced in each case, lighter than the surrounding air, and they accumulate in the upper part of an inhabited room. In ventilating such a room, openings should be made in or near the ceiling for the escape of the impure heated air, while the free admission of fresh air should be secured near the floor.

Exp. 66.—Fasten a piece of taper to a bit of cork, and place it in a plate, with a little water. Light the taper; then cover it with a wide-necked gas jar, and over the neck of the jar place a glass gas-chimney, as in Fig. 23. In a few minutes the taper will burn dimly, and would soon go out; but if the edge of the jar be slightly raised out of the water in the plate, air will enter at the bottom, and the heated impure air will pass off by the chimney. The course of the current may be watched by means of the smoke from a smouldering bit of brown paper, which will follow the movements of the air, if brought near enough. Instead of lifting the edge of the jar,

Fig. 23.



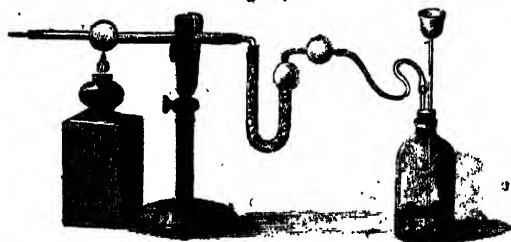
divide the air-way through the chimney by placing a long slip of card down the middle; a downward current will then be established on one side of the card, and an ascending current on the other, and the taper will burn freely.

It is on this principle that small mines are often ventilated for a time, the shaft being divided by a wooden partition into a downcast and an upcast shaft. In the best ventilated mines, however, this is done by two separate shafts, sunk at some distance from each other, and in one of these shafts a fire is kept burning, for the purpose of producing an ascending current of hot air. Ventilation by means of fans driven by machinery is, however, both much safer and more effectual in producing the necessary movement of the air.

Carbon may without difficulty be separated from carbonic anhydride.

Exp. 67.—Cause a current of the gas to pass through a drying-tube containing calcic chloride (Fig. 24), and then through

Fig. 24.



a bulb tube containing a small piece of potassium. Heat the potassium in the gas: it will soon take fire, and burn brilliantly. Let the tube cool, and then plunge it into water.

In this experiment potash is formed in the tube at the expense of oxygen derived from the gas; the alkali is dissolved by the water, and black particles of charcoal become diffused through the liquid.

Exp. 68.—Kindle a strip of magnesium foil, by holding it

with the tongs in the flame of a spirit lamp; and when burning brightly, introduce it into a jar filled with carbonic anhydride. The metal will continue to burn; white flakes of magnesia, mixed with black particles of carbon, will be deposited. Add a little dilute nitric acid: this will dissolve the magnesia, and leave the carbon.

Carbonic anhydride is not only absorbed by limewater, but it is also quickly absorbed by any alkali, such as a solution of potash.

Exp. 69.—Fill a strong graduated test-tube with carbonic anhydride by displacement, and invert it in a deep glass containing mercury, as shown in Fig 8. Then introduce the curved beak of a pipette, filled with a strong solution of potash, beneath the edge of the tube, and blow from the lungs with just sufficient force to drive a few drops of the liquid into the tube. The solution of potash will quickly absorb the gas, and mercury will rise in the tube.

A strong solution of potash is in continual use in the laboratory for separating carbonic anhydride from other gases which, like oxygen, nitrogen, and hydrogen, are insoluble in the potash solution. In this way it is easy to estimate the quantity of carbonic anhydride in respired air.

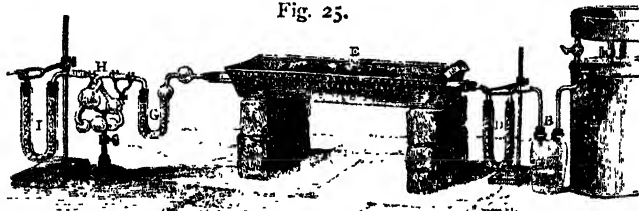
We have thus proved by synthetic experiments that when charcoal is burned in air or in oxygen, carbonic anhydride is formed, and we have found by analysis that the gas contains both oxygen and charcoal. It may be shown that it contains nothing but carbon and oxygen, and the exact proportions may be determined by means of the apparatus shown in Fig. 25.

A is a gas-holder filled with pure oxygen, B a strong solution of potash, C a tube filled with calcic chloride in lumps, D a sheet-iron furnace containing a tube of hard glass: at F, within the tube, is a platinum tray containing the carbon; G is a tube containing calcic chloride, H a series of bulbs filled with solution of potash, while I is a tube filled with lumps of potash.

The platinum tray with the carbon, whether in the form of

diamond, graphite, or charcoal, is weighed accurately at first. Then the oxygen dried in its passage is allowed to stream slowly through the tube, which is gradually made red hot by placing glowing charcoal round it in the furnace. The carbon in the platinum tray burns brilliantly in the stream of oxygen, and becomes converted into carbonic anhydride. The tube should also contain cupric oxide, by which any trace of carbonic oxide which might be formed would be at once converted into the anhydride. This is completely arrested by the potash in the bulb tubes H, no gas but pure

Fig. 25.



and dry oxygen escaping into the air. The gain in weight of H and I together shows how much carbonic anhydride has been formed. The loss of weight of the platinum tray F shows how much carbon has been burnt, and the difference between this weight and that of the carbonic anhydride shows how much oxygen has combined with the carbon. No chemical experiment has ever been made with greater care than this for the purpose of arriving at accurate results, since the composition of carbonic anhydride is a fundamental datum in all analyses of organic compounds. It has been found by repeated trials of this process that 12 grams of carbon require exactly 32 grams of oxygen to convert them into 44 grams of carbonic anhydride; so that, assuming for the present the atomic weight of carbon to be 12, the molecular weight of a carbonic anhydride is 44, and the formula representing its composition is CO_2 .

If carbon be burned in a jar of oxygen over mercury, so as to prevent any loss of the gas, it is found that the gas, when it has cooled down again and is measured with due care, is not altered in bulk. The carbonic anhydride formed occupies the same volume as the oxygen which has entered into its composition, so that the gas contains its own bulk of oxygen.

Carbonic acid, though a weak one, forms a numerous and important series of salts, called *carbonates*. Except those of the alkaline metals, they are nearly insoluble in water; and all, whether soluble in water or not, dissolve with effervescence in dilute nitric acid. The gas which comes off is colourless, with scarcely any smell; and if passed into limewater, it makes it turbid, thus showing it to be carbonic acid.

Many of the carbonates occur in immense quantities as natural products, particularly calcic and magnesian carbonates.

The quantity of carbonic anhydride in the atmosphere is tending continually to increase, in consequence of the numerous chemical processes by which it is being produced; and it would accumulate to a serious extent, were it not prevented by a remarkable counteracting power possessed by growing plants. The green parts of plants, when in the sun's light, decompose carbonic acid, and lay up the carbon in the wood and other parts, whilst they give back most of the oxygen to the air, thus converting again into fuel that material which has been diffused through the atmosphere, and has, by being burned, lost for the time its chemical activity. The rain as it falls dissolves the carbonic anhydride, and carries it down to the earth; and the roots of the plants absorb it, and carry it up into the leaves, where it undergoes the necessary chemical change, so long as the sun's rays fall upon the plant. In the dark, no such removal of carbon from the gas and restoration of oxygen to the air occurs.

Exp. 70.—Into a small gas jar (Fig. 26) fit a good cork, instead of the stopper, and pass a test-tube tightly through a hole bored through the cork. Place the jar in a large beaker filled with

Fig. 26.



spring water, which has been mixed with a fourth of its bulk of solution of carbonic acid in water. Fill the tube with water, and place it in the neck of the jar, having introduced a few sprigs of mint or the leafy branches of any succulent plant in the jar, and then expose it for an hour or two in direct sunshine. Bubbles of gas will be seen studding the leaves; and on shaking the jar, these will become detached, and will rise into the test-tube. After a time the cork and tube may be withdrawn, keeping the mouth of the tube beneath the surface of the water; then close it with the thumb, turn the tube mouth upwards,

and test the gas with a glowing splinter. The wood will burst into a blaze, showing that the gas consists mainly of oxygen.

(18) CARBON: *Symb.* C; *Atomic Wt.* 12; *Sp. Gr.* as diamond, about 3.4.

Carbon is an elementary body of the greatest importance, and it occurs in various familiar forms, viz. naturally as diamond, and as graphite or black-lead, as well as less pure in the different artificial substances known as charcoal and coke. It is also abundant in combination: chalk contains not less than an eighth of its entire weight of carbon, and magnesian carbonate more than one-seventh. Carbon also occurs combined with other elements; for it is the characteristic constituent of those substances which are called *organic* and are of vegetable or animal origin.

a. The *diamond* is the hardest of known substances, and the most valuable of gems. It consists of pure carbon crystallised in forms derived from the regular octahedron and dodecahedron, and often in the form of rolled pebbles, with a dingy exterior, which would cause them often to be over-

looked by an unskilled observer. The diamond can only be cut and polished by grinding it with its own powder. Its most important use is familiar to us in the hands of the glazier for cutting sheets of glass. Owing to its rarity, its high refracting power, and brilliant lustre, it has been prized for ornamental purposes from time immemorial.

Diamond may be burned in oxygen gas, when it consumes away almost without residue. Twelve mgrams. of diamond have been found to yield when thus burned exactly 44 mgrams. of carbonic anhydride, and no other product. It has never been melted. It is a non-conductor of electricity, though other forms of carbon conduct it well. When heated intensely in the arc of the voltaic battery, as soon as it becomes white hot, it swells up, loses its transparency, acquires the power of conducting electricity, and is converted into a black opaque mass resembling coke.

b. Plumbago, or graphite, frequently from its appearance called *black-lead*, though it contains no lead, is another form in which carbon is found naturally, but in tolerable quantity. It has a sp. gr. of about 2.2, and occurs sometimes in crystalline six-sided plates. It has a leaden-grey lustre, leaves a streak upon paper on which it is rubbed, on which account the finest kind is used in making artists' drawing pencils. It is a good conductor of electricity. When it is burned in oxygen, it always leaves from 2 to 5 per cent. of ash, which, however, is not a necessary part of it. The gas which it furnishes when thus burned in oxygen is pure carbonic anhydride. Owing to its perfect indifference to the action of oxygen at common temperatures, it forms a serviceable coating for the protection of ironwork from rust, as is commonly practised with fire-grates and stoves. Graphite, when mixed with clay, is often made into crucibles, because they are not liable to crack in the fire. Molten iron dissolves carbon readily; much of it separates from the iron again if the melted metal is allowed to cool slowly. It is then in the form of graphite.

Pit Coal.—This is one of the most important natural substances rich in carbon. It is a material, of vegetable origin, which has become altered during the lapse of ages, while exposed, under great pressure in the strata of the earth, to the combined action of water holding in solution oxygen derived from the air, and moderate heat. The composition of pit coal varies greatly according to the length of time during which it has been thus acted on, the older deposits being those which contain the largest proportion of carbon. The elements of which the original vegetation consisted are carbon in large proportion, oxygen in smaller quantity, still less hydrogen, and a very small proportion of nitrogen; but besides these there is a variable quantity of saline and earthy substances which always occur in vegetable juices; added to which are earthy impurities derived from the adjacent strata, as well as a portion of iron pyrites (FeS_2), which is always gradually formed in the coal. When coal is burned in the open fire, if there be a sufficient supply of air, the carbon becomes carbonic anhydride, the hydrogen burns into water, the nitrogen escapes chiefly as gas, and the ash which remains is composed of the saline and earthy residue.

Much of the South Wales coal is of the modification called *culm* or *anthracite*, which contains upwards of 90 per cent. of carbon, and but little volatile matter. It burns without flame, and with a steady glow. House coal, such as is used in London, is of a different kind. It softens when heated, and forms a pitchy or bituminous mass, which causes the pieces to cake together. Such coal is never burned completely, even in an open fire; but in the act of burning it gives off a quantity of gaseous or tarry matter, holding finely divided carbon or soot in suspension. When a quantity of fresh coal of this kind is thrown upon a hot fire, it at once begins to be decomposed; considerable quantities of the compounds of carbon and hydrogen are formed, and pass off in the condition of gas or vapour. A portion of these substances immediately takes fire, and burns with a bright light

and a smoky flame; but a large portion of them, when they pass over the glowing embers, is more or less completely decomposed; the carbon and hydrogen become partially separated from each other in a part of the fire where there is but little uncombined oxygen; the hydrogen, being the more combustible element of the two, seizes upon such oxygen as it finds, or else it escapes unburnt in the form of gas; while the carbon, still containing a notable proportion of hydrogen, is carried away in very fine particles, and passes off as smoke, suspended in the heated gases.

The formation of this black smoke may, however, be prevented by throwing the coal upon the fire in small quantities at a time, taking care to keep up a strong steady heat, so as to consume the gases as they are formed; but this can only be secured by a sufficient supply of atmospheric air, a condition not so easily fulfilled in manufacturing furnaces as might be expected, though with proper care it can be done.

When bituminous coal is heated in long closed iron cylinders, out of contact with air, a large quantity of gas and of tar is formed; they contain the oxygen, hydrogen, nitrogen, and part of the carbon of the coal, while the greater portion of the carbon is left behind as a porous mass, called *coke*. Coke resembles graphite in properties, but it retains all the ash and earthy impurities of the coal. It burns with a steady glow, without emitting flame or smoke; it is less combustible than coal, and requires a brisk current of air to keep it burning. The more highly the coke is heated during its preparation, the more compact does it become, the better does it conduct heat, and the more slowly does it burn.

Exp. 71.—Get a blacksmith to weld up one end of a wrought-iron gas-pipe 25 mm. (1 inch) in diameter, and 50 centim. long. Fit a cork and a bent tube to the open end; put from 50 to 100 grams of coarsely broken coal into the iron tube; * heat the

* A hard glass tube may be used instead of the iron tube, and may be heated in a flame, but it does not yield the gas so easily.

closed end in a common fire, and direct the gas into the pneumatic trough. Some tarry matter will pass over, and a considerable quantity of gas may be collected, which will burn with a bright flame. When all the gas appears to have been driven off take the tube out of the fire, let it cool, and then, with an iron rod, detach what is left in the inside of the tube. It will be found to be common coke. Put some of this coke in a small open clay crucible, and heat it in the fire: the coke will gradually burn away, leaving nothing but a little ash.

The dense coke required for burning in the powerful draught created under the boiler of a locomotive engine is usually prepared by burning the coke in massive brick ovens, in each of which several tons of coal can be charred in a single operation, the ovens being provided with a sliding door, for regulating the admission of air, which plays over the surface of the heap and burns off the volatile matters, and so chars the whole mass at a very high temperature, each charge requiring 48 hours for its conversion into coke.

If, instead of heating coal in an iron retort, wood be treated in the same way, a still larger quantity of volatile and liquid products will be given off, and what is left behind is a black porous substance, of the same shape as the wood, familiarly called *charcoal*. Wood tar, vinegar, and wood naphtha are among the liquid products, which redden litmus paper strongly, but the gas has little illuminating power. A more compact charcoal, better suited for use as fuel, is made by burning wood in heaps. A stake is driven into the ground, brushwood is placed round the bottom, and logs of wood are piled up regularly around the stake. The heap thus formed is often 10 metres or more in diameter, it is covered with powdered charcoal, turf, and earth. It is then kindled by introducing lighted fagots at openings left for the purpose. Large quantities of moisture are driven off, and the fire spreads gradually through the mass, the admission of air being carefully regulated, so to cause one part of the wood in burning completely to char and drive off the volatile matters.

from the rest. When gas and vapours cease to come off, the fire is extinguished by closing all the openings for the admission of air, and adding a thicker layer of mould and turf. Such a heap takes nearly a month to burn out, and never furnishes more charcoal than a quarter of the weight of the wood used.

The gas and the liquids which are obtained from the coal and the wood during this process of *destructive distillation* do not exist ready formed in these substances. They are the result of chemical changes produced under the influence of the heat; the carbon and hydrogen combine together in new proportions, and thus furnish substances quite different in properties from the original coal and wood.

Nearly all vegetable and animal matters, when heated out of contact with air, furnish charcoal more or less pure.

Exp. 72.—Put a few pieces of wood into a clay crucible; cover the wood completely with sand, and heat the whole for 20 minutes in a fire. Gas will be given off, and burn. Take the crucible out of the fire, let the whole cool, then empty the crucible: the wood will be found to be converted into charcoal.

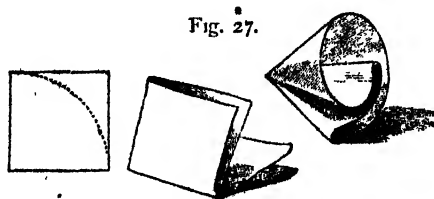
Charcoal gives out more heat in burning than an equal bulk of wood, as the moisture and volatile matters given off by the wood carry away much of the heat in the latent state. But in the economy of fuel it is not sufficient to consider simply the absolute amount of heat which a given weight of it emits in burning. A fuel which burns with flame is necessary where it is desired to communicate an elevated and uniform temperature to objects at a distance from the fire-grate, as in heating glass pots or the contents of a porcelain kiln; whilst in heating boilers and objects where direct radiation from the fuel can act fully, coke, charcoal, or anthracite is very valuable; and in an ordinary open fire these same fuels radiate much more heat into the room, though they do not look so cheerful, as the bituminous coal, with its fitful, flickering flame.

There are other forms of carbon besides coke and charcoal which are manufactured for use in the arts. One of these is *lamp-black*, the basis of printers' ink, and the most permanent of black pigments. It is obtained by heating in an iron pot vegetable matters, such as rosin and pitch, which are rich in hydrogen and carbon. The vapours are burned in a current of air insufficient for complete combustion; the hydrogen, which is the more inflammable element, burns first, leaving the carbon in a finely divided state.

Exp. 73.—Set fire to a little rosin in a small iron spoon; hold a cold white plate in the flame. Abundance of soot will be deposited upon it. The flame of a candle or of an oil lamp will give a similar result.

Animal charcoal, or *ivory black*, is prepared by heating bones in iron retorts. It is used largely by the sugar refiners for removing colour from syrups.

Exp. 74.—Place a few pieces of mutton shank or other bone in a clay crucible; cover them completely with sand, and heat the crucible for half an hour in a common fire. Take it out, and when cold crush the burnt bones to a coarse powder. Dissolve 25 grams of coarse brown sugar into 5 or 6 times its weight of water; divide the solution into two parts, and pour one half upon about 20 grams of the crushed bone charcoal, and let it stand for an hour; then filter the solution through blotting-paper. In order to prepare this filter, fold a square of paper, as



shown in Fig. 27, first into half, and then again into a quarter of its first size; cut off the edges in the direction of the dotted line shown in the left-hand figure, open out the folded paper, and drop it into a funnel a little larger than the paper cone.

The liquor which runs through will be found, when compared with the original syrup, to have lost most of its brown colour, which is caused by a substance that remains adherent to the charcoal. Wash out the syrup; then pour a little solution of potash upon the charcoal in the filter. The brown colouring matter will become again dissolved by the alkaline solution as it runs through.

Port wine, porter, and many other coloured liquids may be deprived of their colour in a similar manner.

Wood charcoal produces decolourising effects similar to those obtained with animal charcoal, though it is less powerful. Charcoal, like most porous bodies, condenses many gases and vapours in its pores.

Exp. 75.—Weigh a piece of freshly burned charcoal as soon as it is cold; leave it exposed to the air for 24 hours, and weigh it again: it will be found to be heavier. Place the charcoal in a glass tube, and heat it over a lamp: a good deal of moisture will be driven off, and will become condensed on the cold sides of the tube. This moisture was absorbed from the air by the charcoal.

Exp. 76.—Place a piece of raw meat in a glass jar, and cover it with a layer of charcoal powder 25 mm. thick, and leave it for several days. No offensive odour will be perceived, even in the height of summer.

The meat may even become putrid, but the noxious and offensive gases which would otherwise escape are absorbed by the charcoal, and are slowly oxidized within its pores by the action of the oxygen, condensed by the charcoal from the surrounding air. Shallow trays of wood charcoal are of use in sick rooms, owing to their exerting this absorbent and purifying action upon the atmosphere. They preserve their power for an unlimited time, the carbon of the absorbed organic matter being dissipated as carbonic anhydride, and the hydrogen as water.

Owing to this absorbent action, charcoal forms a valuable material in the construction of filters for water, as it acts powerfully on many of the organic impurities.

Exp. 77.—Shake up some stagnant water which has been kept till it smells offensively with a little powdered charcoal. In an hour it will have lost all its disagreeable odour.

Carbon is indestructible by exposure, at ordinary temperatures, to the air or to water. Hence it is a common practice to char the surface of wooden piles before driving them, and to prepare the interior of casks and water-butts in a similar manner.

Charcoal and the common varieties of carbon, however, combine rapidly with oxygen at high temperatures; and their attraction for oxygen is so great that carbon in some form or other is employed to remove oxygen from its combinations with other elements, particularly from the oxides of the metals, which, when heated with carbon, are *reduced* or brought back to the metallic state. Hence carbon is spoken of as a *reducing agent* by the metallurgist. This action may be shown as follows:—

Exp. 78.—Mix in a mortar 20 grams of litharge or lead oxide (PbO) with 40 grams of common salt and 1 gram of powdered charcoal; cover it with a little more salt, and place the mixture in a small clay crucible; heat it to bright redness in the fire. When the mixture is melted, take the crucible out of the fire and let it cool. When quite cold, break the crucible, and a bead of lead will be found at the bottom, under the melted salt, the carbon having taken the oxygen from the oxide of lead.

Twelve grams of pure charcoal,* free from ash, when burned in a current of oxygen, yield exactly 44 grams of carbonic anhydride. Equal weights of diamond, plumbago, and charcoal are thus shown, when heated with oxygen, to yield equal weights of carbonic anhydride; and though so different in appearance, they still consist of the same elementary body. Many of the elements have the power of assuming forms which differ in appearance and properties quite as much as these three different conditions of carbon. Such elements are then said to assume different *allotropic*

* Common charcoal, however, always retains a little hydrogen.

states, which is as much as to say that in each different modification, though all the atoms are alike, yet they are arranged in a different way. The atoms of carbon, for instance, which constitute diamond, are arranged very differently from those which form graphite, and the atoms of carbon in charcoal are differently arranged from those of either diamond or graphite.

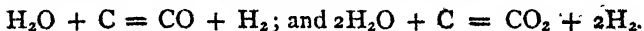
Carbon unites with sulphur if strongly heated with it, and if heated intensely in hydrogen gas a small quantity of acetylene (C_2H_2) is formed; but it has little tendency to unite with the other non-metals. Some of the compounds of carbon with the metals are important. They are termed *Carbides*.

(19) CARBONIC OXIDE: *Symb.* CO; *Atomic and Mol. Wt.* 28; *Sp. Gr.* 0.967; *Rd. Wt.* 14.

Carbon forms only two compounds with oxygen, so far as is known. One of these is carbonic anhydride; the other, also a gas, containing just half as much oxygen, is called carbonic oxide.

Exp. 79.—Fill the iron tube (Fig. 13) with small lumps of charcoal, instead of with iron turnings; make it red hot in the furnace, and drive steam over the ignited charcoal. Collect the gas which is formed: it will burn with a pale blue flame. Shake up a little limewater with another of the jars of gas: it will be rendered milky.

Three gases, viz. hydrogen, carbonic anhydride, and carbonic oxide, are formed in this case. These changes may be thus explained: the carbon takes the oxygen from the water, forming a mixture of carbonic oxide and carbonic anhydride, whilst its hydrogen is set at liberty—



Exp. 80.—Mix some chalk with its own weight of iron filings; place 40 or 50 grams of the mixture in an iron tube arranged as in *Exp.* 71. Heat the closed end of the iron tube to redness in the fire: a gas comes off, which may be collected over water.

The heat expels carbonic anhydride from the chalk, and the iron takes half the oxygen from the carbonic anhydride, and forms carbonic oxide; $\text{CaO}, \text{CO}_2 + \text{Fe}$ becoming $\text{CaO} + \text{FeO} + \text{CO}$.

Exp. 81.—Plunge a taper into a jar of the gas; the light will be extinguished, but the gas will burn at the mouth of the jar with a blue flame.

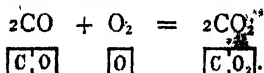
Carbonic oxide is often formed largely in stoves and furnaces, owing to the manner in which heated carbon acts on carbonic anhydride. When air enters at the bottom of a clear fire, the oxygen burns a part of the carbon at once into carbonic anhydride; and this gas, with the nitrogen of the air, passes through the red-hot embers. The nitrogen undergoes no change, but the carbonic anhydride takes up a further quantity of carbon, and becomes converted into carbonic oxide: $\text{C} + \text{CO}_2 = 2\text{CO}$, the carbonic anhydride being exactly doubled in bulk in consequence. This mode of the formation of the gas is important, because, if the supply of air to a furnace is too small, the carbonic oxide passes up the chimney unburnt, and much heat is wasted, which would be saved if the gas were properly consumed. Sometimes we see the carbonic oxide burning on the top of a clear glowing fire, where it again mixes with fresh oxygen of the air while the gas is still hot enough to burn. Furnaces are sometimes made to supply air just above the top of the fire-grate, so as to burn the carbon oxide completely.

Exp. 82.—Make the iron tube and charcoal red hot, as in *Exp. 79*; but instead of sending steam through it, attach to the tube a bottle which is giving off carbonic anhydride steadily. Collect the gas over water as it escapes at the other end: it will burn with the blue flame which distinguishes carbonic oxide.

Exp. 83.—Collect some carbonic oxide in a jar provided with a stop-cock at the top, or fitted up in the way directed in *Exp. 48* (*Fig. 16*), with a flexible tube and screw-tap. Fasten a glass quill tube to the vulcanised tube; depress the jar in the pneumatic trough, and allow a little of the gas to escape, by relaxing the

screw; set fire to the issuing gas, and hold over it a small gas jar. No water will be condensed on its sides; but if the jar be closed with a glass plate, and limewater be poured into it, a white precipitate of chalk will be produced.

The carbonic oxide in burning becomes converted into carbonic anhydride; 2 litres of carbonic oxide require 1 litre of oxygen for its complete combustion, and 2 litres of carbonic anhydride are produced:

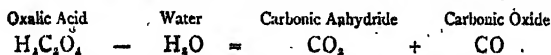


There are several other ways of preparing carbonic oxide. The best of these consists in drying the yellow salt known as potassic ferrocyanide, $\text{K}_4\text{FeC}_6\text{N}_6$, $3\text{H}_2\text{O}$ (prussiate of potash), till it crumbles down to a white powder.

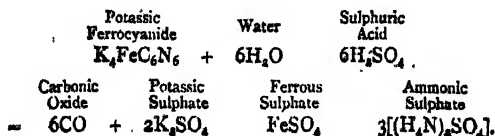
Exp. 84.—Mix 5 grams of this dry powder with 50 c. c. of oil of vitriol in a Florence flask; adjust a cork and a wide bent tube to the mouth of the flask, and heat the mixture. When the heat reaches a certain point, the gas will come off very quickly.

In this experiment the decomposition is complicated,* but the result is, that the whole of the carbon of the salt comes off as pure carbonic oxide, while the whole of its nitrogen remains behind as an ammonium salt with the acid employed.

Another plan commonly practised for obtaining carbonic oxide is to heat crystals of oxalic acid with about 10 times their weight of oil of vitriol; but in this case the carbonic oxide is mixed with an equal volume of carbonic anhydride:

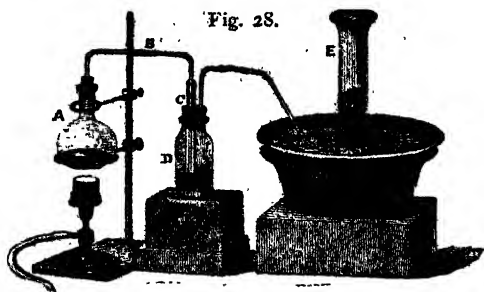


In this process the oxalic acid is deprived of the elements



of water by the sulphuric acid, and the remaining carbon and oxygen pass off in the form of equal measures of the two gases.

The carbonic anhydride may be removed by causing the mixture of gases to pass through a solution of caustic soda ; and the apparatus may be arranged as shown in Fig. 28, in which the gas generated in the flask A is transmitted through



the tube B, which passes loosely through the wider tube C below the surface of a solution of soda contained in the bottle D. From this bottle the gas passes off, by a tube the end of which is above the solution, into the jar E standing in the pneumatic trough.

Carbonic oxide is a gas without colour, but with a faint oppressive odour. It is very poisonous when breathed, so small a quantity as 1 measure of the gas in 100 of air speedily producing a peculiar sensation of oppression and tightness of the head. The fumes of burning charcoal owe their most active poisonous property to the presence of carbonic oxide, which is always largely mixed with carbonic anhydride in the products of a slowly-burning charcoal fire. This gas has not been liquefied, either by cold or pressure. It is but slightly soluble, 100 c. c. of water dissolving about 2·4 c. c. of the gas. A solution of cupreous chloride (CuCl) in hydrochloric acid dissolves carbonic oxide gas slowly if

agitated with it, but the gas is not soluble in a solution of potash.

(20) *Classification of Crystals.*—We have had occasion to allude to the crystalline form of the diamond and some other substances, and different varieties of crystals will continually need notice. It will therefore be necessary to acquire some general notions of what is meant when crystals are spoken of, how their different varieties are designated, and what are the principles on which their different forms are classified.

Exp. 85.—Dissolve 250 grams of nitre in half a litre of boiling water, and allow the solution to cool slowly in a basin. Six-sided needles will gradually be formed in the liquid, owing to the separation of part of the salt.

Exp. 86.—Dissolve some common salt by grinding it with about twice its weight of water in a mortar. Pour off the clear liquid, and set it aside for several days in a soup plate or other shallow vessel: the water will gradually evaporate, and little cubes of salt will be formed.

Exp. 87.—Prepare in like manner a solution of alum, and leave it to evaporate slowly, when transparent octahedra will be obtained.

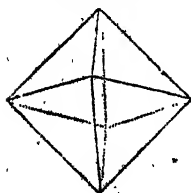
In most cases, where solid bodies are allowed to separate undisturbed from their solutions, they are found to assume the form of some regular geometrical solid, bounded by flat faces, called *planes*. Each substance has its own peculiar form, and the regular geometrical solids thus obtained are called *crystals*. By these differences in form many substances may be at once distinguished from each other. The process of crystallisation is commonly used as a means of freeing salts from small quantities of foreign admixture; as, for instance, for separating nitre from small quantities of common salt. The impure nitre is dissolved in hot water, and the nitre as it cools crystallises, whilst the liquid, or *mother liquor*, retains in solution the small proportion of common salt.

The principle upon which the classification of crystals is founded is the symmetry of their form. By symmetry is meant a complex uniformity of figure; in other words, a

similar arrangement of two or more corresponding forms round a common centre. This, indeed, is the general law of creation. It is seen in the correspondence of external form of the two sides of the body in animals; of the two halves of a leaf on either side of its midrib in plants; in the two halves of most seeds; and still more rigidly in the constitution of every crystal. The imaginary line round which the parts of a crystal are symmetrically disposed is called the *axis of symmetry*, or, simply, the *axis of a crystal*.

Select an octahedral crystal of alum, and place it with one of its angles uppermost; an imaginary line, *aa*, Fig. 29*a*, pass-

Fig. 29.



ing through the middle of the crystal to the opposite angle is an axis of the crystal. Each end of this axis is formed by the meeting of four sides or planes of the crystal. Every one of these sides is similar to its fellows, and each is inclined to the axis at an equal angle. Each of the four faces therefore is symmetrically disposed around the axis.

If any internal force act upon the particles during the formation of the crystal, so as to produce a bevelling of one of the edges of any one of these planes, the same cause will act upon the other corresponding edges, and will produce a corresponding modification of a symmetrical character upon each of the other corresponding edges. This regularity is often interfered with mechanically, as when many crystals are formed in the same mass, or by the accident of its position during its formation.

* In describing crystals, several of these imaginary lines are supposed to exist, around which their faces are arranged. Generally speaking, these axes may be reduced to three, all of which intersect each other in the centre of the figure.

For the purpose of making the direction of these axes more easily understood, let a piece of soap be cut in the form of a cube, or figure of 6 equal square sides, each of

which is 6 or 8 centimetres long; through the middle of one of its sides thrust a piece of wire 18 centimetres long, so that it shall pass out in the middle of the opposite side, and project equally on either side, as shown at *aa*, Fig. 29*a*; do the same through two of the other sides, as at *bb*. These two wires will represent the direction of two out of the three axes of the cube which cross each other at right angles at its centre. Now repeat the process on the remaining two sides. The third axis of the cube will be represented by this third wire, which will be at right angles to both the others.

Fig. 29*a*.

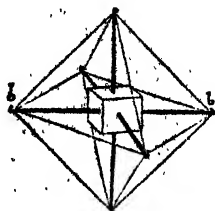


Fig. 30.

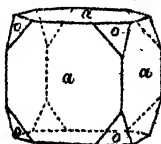


Fig. 31.

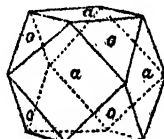
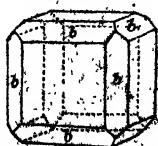


Fig. 32.



Twist a piece of thread round the end of one of the wires, and connect each point of the wires in succession with each of the four points nearest to it, stretching the thread across from one to the other. An outline of the regular octahedron will thus be formed. Take another cube of soap, and pare off each of its 8 corners, as at *oo*, Fig. 30, by a plane inclined equally to each of the three adjacent faces of the cube. If these new faces be gradually enlarged by continuing to pare away the corners, as shown in the Figs. 31 and 32, the cube will by degrees be converted into the octahedron (Fig. 36), an 8-sided solid, in which the three axes of the cube, *aa*, *aa*, *aa*, end in the six solid angles of the octahedron. If in another cube of soap the 12 edges

Fig. 33.



of the cube be pared off so as to form 12 planes, b, b , Fig. 33, sloped equally towards the adjacent faces, the cube will gradually be converted into a regular 12-sided figure, the rhombic dodecahedron (Fig. 34), which is also symmetrically

Fig. 34.

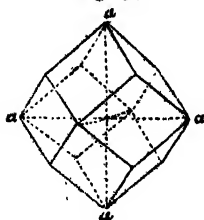
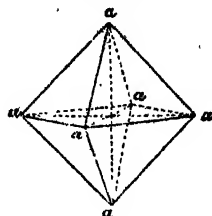


Fig. 35.

Fig. 36.



arranged around the three axes of the cube (Fig. 35). These three forms, the cube, the octahedron, and the rhombic dodecahedron, being formed around a similar set of axes, are said to belong to the same system of crystals; and this particular system is called the *regular* or *cubic* system. All the different known forms of crystals have been arranged in one or other of six such systems or classes, viz.:—

1st. The regular or cubic, distinguished by possessing three axes equal in length, crossing each other at right angles. Common salt and fluor spar, which crystallise in cubes, alum in octahedra, and garnet in the rhombic dodecahedron, are examples of this class.

2nd. The *square prismatic* or *pyramidal*.—In this system

Fig. 37.

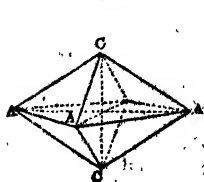


Fig. 38.

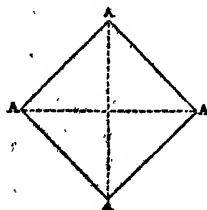
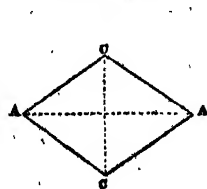


Fig. 39.



there are also three axes, which cross each other at right angles; two of these axes are equal, but the third or principal axis is either longer or shorter than the others. The forms of this system are either (1) the octahedron (Fig. 37),

Fig. 39 a.



Fig. 40.

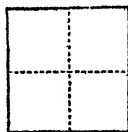


Fig. 41.



such as potassic ferrocyanide, which sometimes loses the pointed terminations and becomes shortened into the form of a table, or flat, plate; or (2) the square prism, sometimes ending in the faces of the octahedron, as tin-stone (Fig. 40). The base of the octahedron is shown in Fig. 38, with its two equal axes, AA , AA , terminating in the angles; but there are octahedra in which the two axes terminate in the middle of the sides, as shown in Figs. 39, 39 a, in which, in Fig. 39, the principal axis, CC , is seen intersecting one of the others.

3rd. The *rhombohedral* or *hexagonal* system.—There are four axes in this system: three of these are in the same plane or flat surface; they are equal in length, and cross each other at angles of 60° , as shown in Fig. 41; while the fourth or

Fig. 42.

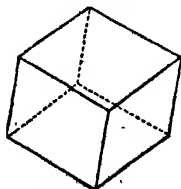


Fig. 43.

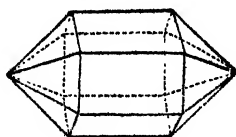


Fig. 44.

principal axis crosses the other three at right angles, and may be either longer or shorter than they. The six-sided prism, like beryl (Fig. 42), and the rhombohedron, such as Iceland spar (Fig. 43), are the most important forms, some-

times conjoined with the double six-sided pyramid which usually terminates the crystals of quartz (Fig. 44).

4th. The *prismatic* system.—In this there are three axes, AA , BB , CC , all unequal in length, but they all cross each

Fig. 45.



Fig. 46.

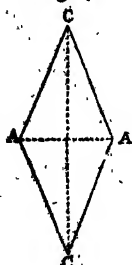


Fig. 47.

A

other at right angles. Two of them form a rhombic base for the prism or octahedron, as shown in Figs. 45, 46, 47, the dimensions of the rhomboid varying according to the length of each pair of axes included in the section.

Fig. 48 represents an octahedron of this system, to which sulphur crystallised in the cold belongs. Fig. 49 represents a tabular prism of this class.

5th. The *oblique* system.—In this there are three axes, which may all differ in length; two of them cross each other obliquely, as is shown in the principal section of the octahedron (Fig. 51), while the other crosses them both perpendicularly, as shown in Fig. 52. The octahedron itself is seen at Fig. 50. The principal forms are the oblique rhombic

Fig. 48.

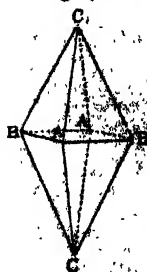


Fig. 49.



Fig. 50.

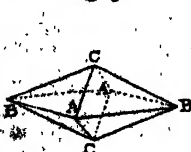
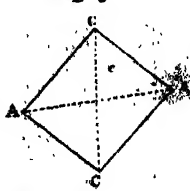


Fig. 51.



prism, a modification of which is seen at Fig. 52a. Sulphur crystallised after fusion, sodic sulphate, and borax belong to this system.

6th. The *doubly oblique* system. This is the most complicated of the whole series. The three axes may all differ in length, and they cross each other obliquely. Cupric

Fig. 52.

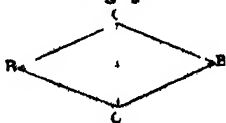


Fig. 52a.



sulphate and bismuth nitrate offer good examples of the doubly oblique prism, one modification of which is shown in Fig. 53, while the octahedron is seen in Fig. 54.

Fig. 53.



Fig. 54



Inorganic bodies which are destitute of crystalline form are said to be *amorphous*. When, like carbon, they crystallise in forms which belong to two distinct crystalline systems, they are said to be *dimorphous*, and when with a similar chemical composition they crystallise in similar forms, as is the case with the arseniates and phosphates of the same metal, or the seleniates and sulphates of the same metal, they are said to be *isomorphous*.

NOTE—A *prism* is a solid, the lateral edges of which are parallel, and the terminal planes of which are also parallel. Prisms which stand perpendicularly when resting on their bases are called *right* prisms, those which incline from the perpendicular are called *oblique* prisms. When the base is a rhomb, or a rhomboid, it is called a *rhombic* prism, and a rhombohedron is a six-sided solid, all the sides of which are formed by rhombs, a rhomb being a plane figure with four equal parallel sides, but the angles of which are not right angles, while a rhomboid is a similar figure in which one pair of sides is longer than the other pair.

CHAPTER V.

OXIDES OF NITROGEN—NITRIC ACID—AMMONIA.

(21) NITRIC ACID: *Symb.* HNO_3 ; *Atomic Wt.* 63; *Sp. gr. of liquid*, 1.52; *Boiling Pt.* 84.5°C. ; *Freezing Pt.* about -40°C.

The attraction of oxygen for nitrogen is but feeble; these gases do not easily combine together, and they remain mixed together without change and under great variation of conditions in atmospheric air. Nevertheless, true chemical compounds may be formed between them, differing entirely in properties from the bland mixture which we breathe at every moment. As in many other cases where the attraction between two elements is weak, nitrogen forms with oxygen several compounds, not fewer than five being known: they contain 1, 2, 3, 4, and 5 volumes of oxygen respectively, uniting in each case with $\frac{1}{2}$ volumes of nitrogen.

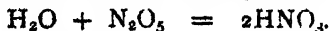
These compounds have been named—

1. Nitrous Oxide . . . N_2O
2. Nitric Oxide . . . N_2O_3 or NO
3. Nitrous Anhydride . . . N_2O_3
4. Nitrogen Peroxide . . . N_2O_4 or NO_2
5. Nitric Anhydride . . . N_2O_5

The third of these oxides, when dissolved in water, furnishes nitrous acid (HNO_2), for



and the fifth yields nitric acid (HNO_3), since



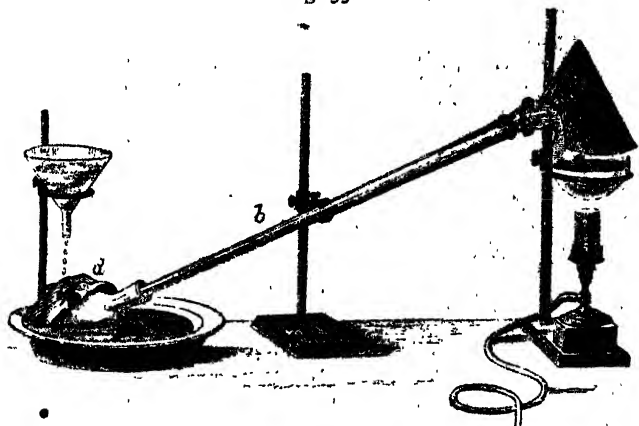
Nitric acid is one of the most important acids known. It was formerly called *aqua-fortis* (strong water), from its corrosive action and power of dissolving the metals.

Traces of nitric acid are always formed when a discharge of electricity passes through moist air, so that rain water generally contains a trace of this acid, owing to the action of lightning or atmospheric electricity. But in tropical

climates, particularly in some districts of India, potassic nitrate, and in Chili sodic nitrate, is found as an efflorescence upon the surface of the soil. It is from one of these salts that nitric acid is extracted for use in the arts. The operation may be conducted on a small scale as follows:—

Exp. 88.—In a retort, *a*, Fig. 55, which will hold 2 litres place half a kilogram of sodic nitrate,* and pour over it an equal weight of concentrated sulphuric acid. Adjust the retort to a Liebig's condenser (Fig. 11), or even to a long straight tube, as shown at *b*, and cover the upper part of the retort with a tinplate

Fig. 55.

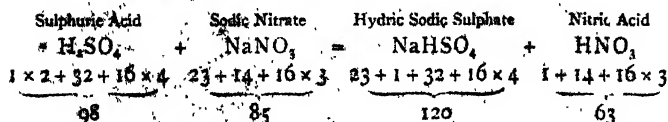


cap, *c*, for the purpose of keeping the body of the retort hot, and distil the mixture carefully over an Argand gas-burner, collecting the intensely corrosive acid liquid in a flask cooled by immersion in a pan of water. This experiment is best made in an outhouse where there is a free current of air. Red fumes come off, and a straw-coloured liquid distils over, which is concentrated nitric acid, or *hydric nitrate*, as it is now sometimes called.

In this distillation the kind of change called 'double

* In making the acid, smaller quantities may be used, and saltpetre or nitre (the potassic nitrate, KNO_3) may be employed instead of sodic nitrate.

decomposition takes place; part of the hydrogen of the sulphuric acid changes place with a corresponding amount of the sodium of the sodic nitrate, forming hydric sodic sulphate, which, as it is not volatile, remains in the retort, while the more volatile nitric acid distils over when heated. The decomposition may be thus represented:



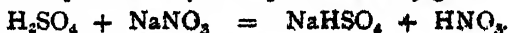
This plan of obtaining nitric acid from one of its metallic salts affords a good instance of the method adopted generally when volatile acids which can be distilled without suffering decomposition are required. The weaker and more volatile acid is in such cases displaced, like the nitric, by the stronger and less volatile acid, such as the sulphuric; and in the process the hydrogen of the stronger acid changes place with the metal contained in the salt of the acid sought. The ordinary acids, it must be remembered, are always *salts of hydrogen*.

When nitric acid is distilled in glass vessels, the quantity of sulphuric acid used is double that required by the manufacturer, who employs a large iron cylinder, the upper part of which is lined with fire-clay to protect it from the action of the acid vapours; but it requires a higher heat to drive off the last portions of the nitric acid.

In fact, sulphuric acid forms two different salts with sodium, one of which is an *acid* sulphate, and the other a *neutral* sulphate; the neutral sulphate containing twice as much sodium as the other. The acid sulphate, or hydric sodic sulphate (NaHSO_4) is very soluble and readily fusible, so that it can be extracted from the glass retort without risk; while the neutral sulphate (Na_2SO_4) is less soluble, and cannot be melted in glass vessels.

When sodic nitrate and sulphuric acid are mixed in the

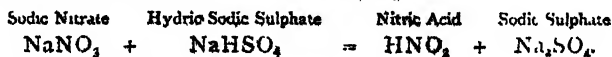
proportion of equal weights, the whole of the nitre is decomposed in one stage; the acid salt only is obtained, and nitric acid comes over at a low temperature; half the hydrogen only of the sulphuric acid being displaced by sodium. The change is represented by the equation already given—



But if the nitrate be mixed with half its weight only of sulphuric acid, the decomposition takes place in two stages, instead of in one. In the first of these, *half the nitre* only is decomposed, hydric sodic sulphate being produced at first, as before, and a gentle heat is sufficient to distil over this first half of the nitric acid—



As soon as the first half of the nitric acid has come over, the heat must be increased; the acid sulphate will then begin to act upon the undecomposed nitre; the second half of the nitric acid is now formed, but is partly decomposed, particularly towards the end of the process. The whole of the sodium remains in the retort in the form of disodic sulphate, or the neutral sulphate. This second ~~stage~~ of the distillation may be represented by the following equation—



The acid which is distilled in this way has a yellow colour, owing to the presence of one of the lower oxides of nitrogen in solution; but the pure acid is quite colourless. Its exact analysis cannot easily be made. It is very easily decomposed. The sun's light causes it to change, and give off oxygen gas, while the acid becomes yellow or brown. It is a fuming intensely corrosive liquid, which stains the skin of a permanent yellow. It freezes at about -40°C ., and begins to boil at 85.5°C .

Nitric acid is a powerful oxidising agent.

Exp. 89.—Place a little warm powdered charcoal in a small saucer, and pour over it about a teaspoonful of the strongest

nitric acid from a test-tube fastened to the end of a stick : the charcoal will burn with sparks.

Exp. 90.—Fasten a test-tube to the end of a stick, and mix in the tube about 2 c. c. of nitric acid with an equal measure of concentrated sulphuric acid. Place about 2 c. c. of oil of turpentine in a small cup, under the chimney, and pour the acid into the turpentine at arm's length : the mixture will burst into a blaze.

Exp. 91.—Mix the strong acid with about an equal bulk of water ; pour 2 or 3 c. c. of the mixture upon a few copper turnings : dense red fumes will be given off, and the copper will be dissolved, forming a blue solution of cupric nitrate.

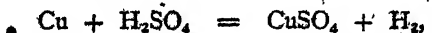
Iron filings, tin foil, and many other metals, when in a divided state, are acted upon by nitric acid with almost equal violence ; indeed, this acid dissolves or attacks nearly all the common metals, except gold and platinum. The mode of its action varies according to the temperature and the degree of its dilution with water. Usually it acts most powerfully when of a sp. gr. between 1.25 and 1.35, or when the strong acid is mixed with from two-thirds of its bulk to an equal bulk of water.

Action of Metals on Acids.—When the common metals are presented to any of the stronger acids a brisk action frequently occurs, accompanied with escape of gas. In all but a few cases the first action of the metal consists in setting free the hydrogen of the acid, which is replaced by the equivalent quantity of the metal, thus forming a *salt* ; for example, zinc and sulphuric acid yield hydrogen and zinc sulphate— $\text{Zn} + \text{H}_2\text{SO}_4 = \text{H}_2 + \text{ZnSO}_4$.

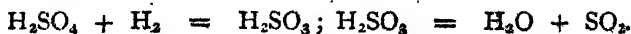
It is not always, however, that the hydrogen thus displaced is evolved as such ; if the conditions be favourable it often reacts, at the moment of liberation, on the excess of acid present ; thus, by the action of copper on strong sulphuric acid, which only takes place on heating, no hydrogen is evolved, but cupric sulphate, water, and sulphurous anhydride are formed—



This reaction doubtless occurs by two stages : at the first cupric sulphate is formed and hydrogen liberated—



but this hydrogen, which has no appreciable reaction on cold sulphuric acid, is able to attack the strongly heated acid, and at once deprives it of a portion of its oxygen, reducing it to sulphurous acid, which further splits up into the anhydride and water :



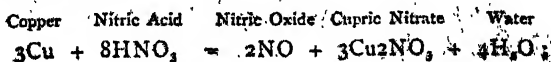
Nitric acid being a powerful oxidising agent, i.e. a body which readily gives up oxygen, never yields free hydrogen when acted upon by metals, but is more or less reduced (deprived of oxygen) by the nascent hydrogen.

Exp. 92.—Act upon zinc or iron with dilute sulphuric acid and collect the gas evolved ; it will burn on the application of flame, and is, in fact, hydrogen. Now add, drop by drop, dilute nitric acid : the evolution of gas ceases, but the metal continues to dissolve ; the hydrogen combines with the elements of nitric acid to form water and ammonia. The latter may be detected at the close of the experiment by adding sodic hydrate to alkaline reaction, and heating, when the smell of ammonia will be apparent.

The successive reactions which may be supposed to occur in the production of nitric oxide, for example, by the action of copper, or mercury, on nitric acid will be evident from the following equations :



Collecting these in one we obtain as expression of the entire reaction—



but it is evident that this equation affords no insight into the course of the reaction.

The primary reaction of a metal on an acid may be considered identical in all cases, and to consist in the formation of the corresponding salt and hydrogen; the secondary reactions which occur, which generally consist in the reduction of a portion of the acid, depend entirely on the nature both of the acid and the metal employed, on the state of concentration of the acid, and on the temperature at which the reaction takes place. Thus by the action of various metals on nitric acid we may obtain at will either ammonia, nitrogen, nitrous oxide, nitric oxide, or nitrogen peroxide.

By the action of metallic oxides on nitric acid the corresponding nitrates and water are formed—



The nitrates are all freely soluble in water; when heated they decompose, leaving a residue of the oxide of the metal and giving off oxides of nitrogen and oxygen; when thrown on red-hot charcoal deflagration (or burning with violence) ensues owing to the rapidity with which they give up oxygen to the burning charcoal.*

(22) *Other Oxides of Nitrogen.*—**NITROUS OXIDE** (or *Nitrogen Protoxide*): *Symb.* N_2O ; *Atom. and Mol. Wt.* 44, *Mol. Vol.* ; *Sp. Gr.* 1.527; *Rd. Wt.* 22.

If pure nitric acid be neutralised by ammonium carbonate, and the solution be evaporated to dryness, a solid white salt is left, ammonium nitrate ($\text{H}_4\text{N}, \text{NO}_3$).

Exp. 96.—Heat a small quantity of this salt in a test-tube: it will melt, and, if heated more strongly, will appear to boil, giving off a considerable quantity of steam, and will at length be wholly dissipated. If a cork and bent tube be adjusted to the mouth of the test-tube, a gas may be collected over warm water.

The ammonium nitrate is entirely decomposed by heat into water and nitrous oxide gas, $\text{H}_4\text{N}, \text{NO}_3$ becoming

* For detection of Nitric Acid, see Appendix.

$2\text{H}_2\text{O} + \text{N}_2\text{O}$. Nitrous oxide gas is colourless and transparent, and has a faint sweetish smell and taste. It is unfit for the support of life, but may be breathed for a time; and it exerts a remarkable action upon the brain and nerves. If respired in a pure state, it produces transient insensibility, and is in consequence sometimes administered to deaden the pain in surgical operations. If it be mixed with air, and breathed for a few minutes, it occasions a peculiar kind of intoxication, often attended with uncontrollable laughter: this has given to the compound its popular name of laughing gas; the effect soon passes off.

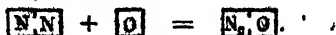
Many bodies burn in nitrous oxide nearly as brightly as in oxygen gas, the nitrous oxide being decomposed into its elements by the burning body.

Exp. 97.—Fill a small jar with the gas, and thrust into it a splinter of wood of which the end is still glowing brightly; it will burst into flame.

Exp. 98.—Place some sulphur in a deflagrating spoon; kindle the sulphur, and when burning briskly introduce it into the gas: it will burn with a pale rose-coloured flame.

Exp. 99.—Half fill a test-tube with gas, over water. Close the tube under water firmly with the thumb, and then agitate the water and gas together. On removing the thumb under water, a considerable rush of water into the tube will occur, as the gas is soluble in about its own volume of cold water. By this circumstance the gas is easily distinguished from oxygen.

Nitrous oxide contains its own volume of nitrogen united with half its volume of oxygen, the three measures which the two gases occupied when separate becoming condensed into two measures by combining—

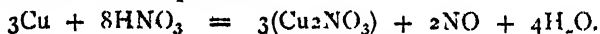


If the gas be mixed with its own bulk of hydrogen in a eudiometer, and the electric spark be passed, an explosion will occur, the bulk of the gas will be reduced to exactly one-half, a few drops of water will be formed, and pure nitrogen will be left equal in bulk to the nitrous oxide employed, $\text{N}_2\text{O} + \text{H}_2$ becoming $\text{N}_2 + \text{H}_2\text{O}$.

NITRIC OXIDE: *Symb.* NO; *Atomic and Mol. Wt.* 30; *Sp. Gr.* 1.039; *Rel. Wt.* 15; *Atomic and Mol. Vol.* .

Exp. 100.—Dilute nitric acid with water until it becomes of the sp. gr. 1.2, and pour about 60 cub. centim. of it upon 15 grams of copper clippings, contained in a retort: the retort becomes quickly filled with red fumes, and a colourless gas may be collected over water.

In this experiment 3 molecules of copper and 8 of nitric acid being concerned, whilst as the result, 3 molecules of cupric nitrate, 2 of nitric oxide, and 4 of water are formed, as shown in the equation:



Other metals, such as mercury, may be substituted for copper in this reaction, and the gas will still be formed.

Nitric oxide has a strong disagreeable odour; it cannot be breathed, even in very small quantity, without producing an instant feeling of suffocation. It is very slightly soluble in water; but its most remarkable property is its strong tendency to combine with oxygen.

Exp. 101.—Allow a bubble or two of the colourless gas to escape into the air: dense brownish-red fumes are immediately formed.

These fumes are always produced when the gas is first prepared in the flask, owing to its action on the oxygen of the air contained in it; they consist of a mixture of nitrous anhydride and of nitrogen peroxide, and are freely soluble in water, with which they form an acid liquid. This change of colour, produced by mixing nitric oxide with any gas containing free oxygen, often affords a convenient means of detecting small quantities of oxygen when present in admixture with other gases, such, for instance, as coal gas.

Exp. 102.—Fill a small gas jar with water coloured blue by means of tincture of litmus, and pass up into it sufficient nitric oxide gas to fill about one-third of the jar: the litmus will not change in colour. Now allow a few bubbles of oxygen to pass up into the nitric oxide: deep red fumes are formed, which are

quickly dissolved, and the blue solution becomes red. If both the oxygen and the nitric oxide be pure, it is possible, by cautiously adding the oxygen, to cause a complete absorption of both gases.

Many combustible bodies, if strongly heated, burn well in this gas; but they are extinguished if not heated sufficiently to begin the decomposition of the gas by separating the oxygen from the nitrogen.

Exp. 103.—Place a piece of dried phosphorus in a deflagrating spoon; kindle it with a hot wire, and instantly introduce the phosphorus into a jar of nitric oxide: it will be extinguished. Again draw it out into the air: it will burst into flame. When burning briskly, again put it into the jar of gas: it will now burn nearly as vividly as in pure oxygen.

Nitric oxide, in contact with strong nitric acid, is immediately dissolved by it. The acid becomes first yellow, and, if more gas be added, ultimately green. It is also quickly dissolved by a solution of ferrous sulphate, forming an intense olive-brown liquid. This fact is often taken advantage of in testing for nitric acid or for nitrates (*Exp. 94*).

Nitric oxide contains equal bulks of its component gases: 1 litre of oxygen, when united with 1 litre of nitrogen, forms 2 litres of nitric oxide—



the gases having united without undergoing any change in bulk.

If potassium or tin be heated in the gas with proper care, the metal is oxidized, and exactly half the quantity of the gas employed is left. This residue is found to be pure nitrogen.

Nitric oxide has never been liquefied.

Nitrous Anhydride (N_2O_3) is the third in the series of the oxides of nitrogen. It may be formed by mixing 4 measures of nitric oxide with 1 measure of oxygen, when deep red fumes are produced. These furnish an acid liquid when dissolved in water—



This acid, the *nitrous*, furnishes, when neutralised by bases,

a series of salts, called *nitrites*; but they are of little practical importance.

Nitrogen Peroxide (NO_2 or N_2O_4) is the fourth term of this remarkable series of oxides. It is most easily procured by heating lead nitrate in a glass tube. Deep red fumes are given off. These fumes may, at a low temperature, be condensed into a red liquid, and, if quite free from water, may even be obtained in crystals. The lead nitrate yields oxygen and lead oxide, as well as nitrogen peroxide, $2(\text{Pb}_2\text{NO}_3)$ becoming $2\text{PbO} + 2\text{N}_2\text{O}_4 + \text{O}_2$. (See Appendix.)

(23) AMMONIA: *Symb.* H_3N ; *Atomic Wt.* 17; *Atomic and Mol. Vol.* ; *Sp. Gr.* 0.59; *Rel. Wt.* 8.5.

Nitrogen and hydrogen cannot be made to unite directly with one another, but they combine indirectly under various circumstances. Only one compound between them can be isolated, and this is the well-known volatile alkali ammonia, or hartshorn.

Exp. 104.—Heat a tuft of hair in a test-tube. it will become brown, and will give off a few drops of an offensively smelling liquid, which will immediately turn a piece of reddened litmus paper blue, owing to the formation of ammonia.

Shreds of bone, of ivory, of isinglass, of horn, of parchment, of feathers, or of silk, and most other animal bodies which contain nitrogen, when thus decomposed by heat, give off a mixture of various compounds of ill-odour, among which ammonia, in greater or less quantity, is always present.

It was by the distillation of substances of this kind that ammonia was formerly exclusively procured, but now it is usually obtained from the waste liquors collected during the distillation of coal in the manufacture of gas, since all coal contains small quantities of compounds of nitrogen, which furnish ammonia when distilled at a high temperature.

Whenever moist animal substances putrefy, ammonia is amongst the products. It is abundant in stale urine, as well as in guano, which is the decomposed excrement of sea-fowl.

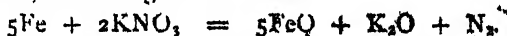
Exp. 105.—Mix intimately 3 grams of fine iron filings in a mortar with 0.2 gram of caustic potash; introduce the mixture into a test-tube, to the mouth of which a cork and a bent quill tube are attached. Heat the mixture in a Bunsen gas flame: gas will escape, and may be collected over water in a test-tube. It burns with flame, and consists of hydrogen.

At a high temperature, the iron displaces hydrogen from the caustic potash—



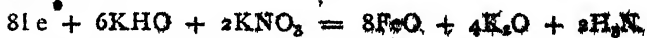
Exp. 106.—Mix 3 grams of iron filings intimately with 0.2 gram of nitre. Heat the mixture and collect the gas as before: it will not burn, does not render limewater milky, and is, in fact, nitrogen.

The iron has combined with the oxygen of the nitre, potash is formed, and nitrogen is liberated—



Exp. 107.—Mix 6 grams of iron filings with 0.2 gram of caustic potash and 0.2 gram of nitre, and heat the mixture in a tube.

The gas which now comes off has the pungent smell of hartshorn, it is strongly alkaline, and immediately restores the blue colour of reddened litmus. In the reaction which takes place, the hydrogen and the nitrogen, at the moment that each is set free, seize one upon the other, and ammonia is formed—



Traces of ammonia exist in the atmosphere, and are brought down in rain and dews to the surface of the earth. In the rusting of iron, and in almost every other process of oxidation when moisture is present, small quantities of ammonia are formed.

The common mode of preparing ammonia for experiment consists in heating one of its commercial salts, such as the sulphate or the hydrochlorate, with a strong base, like lime. The lime combines with the acid, and sets the ammonia at liberty.

Exp. 108.—Powder finely 30 grams of sal ammoniac, and mix it with 20 grams of finely powdered lime : the pungent fumes of ammonia immediately begin to escape.

Fig. 56.



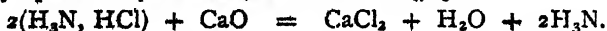
Place the mixture in a flask provided with a cork and a drying tube filled with quicklime and attached to a bent tube (Fig. 56). Apply a gentle heat, and ammoniacal gas will be liberated.

Ammoniacal gas is very soluble in water, which at 15° C. dissolves upwards of 700 times its bulk of the gas ; so that it cannot be collected over water without being absorbed. It may, however, be collected over mercury.

Exp. 109.—Fill a strong test-tube with mercury, close it with the thumb, and invert it in a small basin of mercury over the end of the gas-tube.

Bubbles of gas will rise in the tube, and will displace the mercury.

Ammonia is much lighter than the air ; and this fact may be taken advantage of so as to collect it in a flask or bottle, by upward displacement, as shown in Fig. 56—



It may easily be ascertained when the bottle is full of the gas by the brown colour given to a piece of dry turmeric paper brought near to the mouth.

Ammonia is a gas which has no colour ; it has an intensely pungent odour, and brings tears into the eyes. It has an acrid taste. It is a strong stimulant to the nerves, and, in the form of smelling-salts, is used to check feelings of faintness. It is powerfully alkaline.

Exp. 110.—Place a little solution of litmus, feebly reddened by the addition of a drop or two of any acid, in a basin ; carefully raise the flask full of ammonia gas from the gas-delivering tube ; close the flask with the thumb, plunge the mouth under the

solution of litmus, and withdraw the thumb; the liquid will rush rapidly into the flask, the ammonia gas will be absorbed, and the red liquid will become blue.

Ammonia neutralises the most powerful acids, and forms with them an important series of salts, some of which will be noticed when speaking of the salts of the metals of the alkalis. Any volatile acid, when brought into an atmosphere containing ammonia, produces a white cloud, by combining with the ammonia and forming a white solid salt. This property is often used to detect small quantities of ammonia.

Exp. 111.—Mix common hydrochloric acid with half its bulk of water; dip a glass rod into the mixture, and hold it near the mouth of the flask which is giving off ammonia. Dense white fumes of sal ammoniac will appear around the rod.

Gaseous ammonia becomes liquid at a cold of -40°C ., and by a pressure of about 7 atmospheres at 15° . It may even be frozen at -75°C . into a transparent solid.

Exp. 112.—Slip a piece of freshly-burned charcoal under the edge of a long tube previously filled with dry ammonia gas, and standing over mercury. The charcoal will quickly absorb the ammonia; if pure, the whole of the gas will disappear, and the mercury will fill the tube.

Charcoal has this power of absorbing all gases to a greater or less extent; but such gases as are freely soluble in water are more easily absorbed by charcoal than those which are sparingly soluble. One c. c. of boxwood charcoal will take up fully 90 c. c. of ammonia; so that the gas is subjected to a much greater degree of condensation by this absorptive action than would be necessary to liquefy it by pressure.

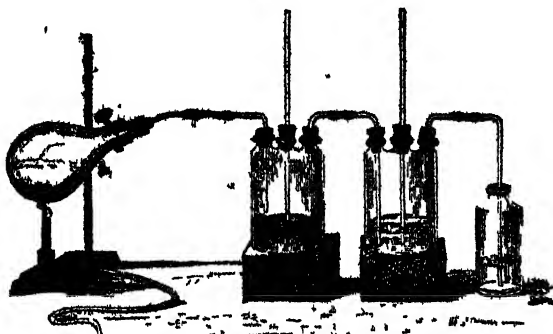
A solution of ammonia is in constant use in the laboratory. It may easily be prepared as follows:—

Exp. 113.—Mix from 30 to 50 grams of powdered sal ammoniac with an equal weight of slaked lime, and place the mixture in a flask; then add 30 or 40 c. c. of water, and let the flask be fitted with a good cork and bent tube, as shown in Fig. 57. Next, by means of a piece of vulcanised tubing, connect the bent

Solution of Ammonia.

tube of the flask with a three-necked bottle containing water, or with a wide-mouthed bottle fitted with a cork and three tubes, two of which are bent at right angles. Neither of these bent tubes must dip into the water. The second bent tube may pass

Fig. 57.



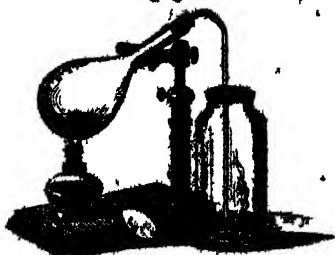
into another three-necked bottle containing water, the first bent tube of which passes below it, and the second bent tube into a bottle also containing water, for the purpose of condensing any of the gas which may escape from the first two vessels.

A bottle of this kind is known as a *Woulfe's bottle*; and the middle tube, open at both ends and dipping into the liquid, is intended to admit air, if the gas is absorbed by the water faster than it is supplied; at the same time, none of the gas can escape through it into the atmosphere. By this contrivance air can enter the partial vacuum, and the water in the outermost bottle is prevented from being driven back by atmospheric pressure.

The solution of ammonia is lighter than water, the specific gravity of the solution diminishing as the quantity of gas contained in it increases. The water also increases in bulk as it dissolves the ammonia; and when saturated at 45° , it contains more than a third of its weight of the alkali. It has the intensely pungent odour of ammonia; and, when gently heated, gives off the gas in large quantity.

Exp. 114.—Boil a little of a strong solution of ammonia in a flask provided with a cork and tube, bent as shown in Fig. 58: the gas will come off freely. Apply a light to the issuing gas: it will not burn readily, but a pale greenish flame will play over the top of the light. Place the tube from which the gas is escaping in a bottle of oxygen, and then apply a light: it will now burn with a green flame.

Fig. 58.



Ammonia consists of one measure of nitrogen and three measures of hydrogen, which become condensed into the space of two measures by the act of combining—



Ammonia may be separated into its two constituent gases by passing a series of electric sparks through a quantity of gaseous ammonia confined in a tube over mercury. By degrees the volume of the gas becomes doubled; and on then causing a little water to pass up into the tube by means of a bent pipette (Fig. 8), the gas will be found to be no longer soluble in water: and on applying a lighted match, the hydrogen in the mixture will take fire. The quantity of hydrogen may be ascertained by introducing (say) 8 measures of the gas obtained by the action of the electric sparks upon ammonia into a eudiometer, and then adding 3 measures of oxygen. On firing the mixture by the electric spark, the 11 measures of gas will become reduced to 2; 9 measures of a mixture of oxygen and hydrogen in the proportions to form water will have disappeared—in other words, 6 measures of hydrogen will have combined with 3 of oxygen, and become condensed as water. Consequently, 8 measures of the mixed gas from the ammonia must have consisted of 6 measures of hydrogen and the 2 of nitrogen which are left.

CHAPTER VI.

SEA SALT—HYDROCHLORIC ACID.

1. CHLORINE. 2. BROMINE. 3. IODINE. 4. FLUORINE.

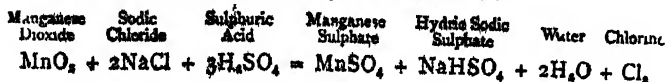
(24) The four elementary bodies, chlorine, bromine, iodine, and fluorine, constitute a remarkable group of closely related substances. Characterised by high chemical activity, and by the power of forming with the metals compounds analogous to sea salt, they have hence been called *halogens*, or salt producers, from $\alpha\lambda\gamma$, sea salt.

1. CHLORINE: *Symb.* Cl; *Atomic Wt.* 35.5; *Mol. Wt.* 71; *Atomic Vol.* \square ; *Sp. Gr.* 2.435; *Rel. Wt.* 35.5; *Mol. Vol.* \square (Cl_2).

Common table salt, or sodic chloride (NaCl), is the most abundant compound of chlorine. It is from this substance almost exclusively that chlorine is obtained; it is never found uncombined in nature.

Exp. 115.—Mix 32 grams of finely powdered manganese dioxide with an equal weight of common salt. Introduce them into a flask provided with a cork and bent tube, and pour upon the mixture 84 c. c. of vitriol previously diluted with 60 c. c. of water and allowed to cool. On heating the mixture gently, chlorine comes off as a dense greenish-yellow suffocating gas, and may be collected in dry bottles by downward displacement.*

The chemical reactions may be thus shown:



Owing to the yellow colour of the gas, it can easily be seen when the bottle is full. Each bottle, as it becomes filled

* The experiment should be made either in an outhouse or under a chimney where there is a strong draught to carry off the irritating vapours.

with the gas, should be closed with a ground stopper, the side of which should be greased. If the gas is collected over water, much is wasted, owing to its solubility in this liquid. Chlorine cannot be collected over mercury, as it immediately begins to combine chemically with the metal.

Another process for obtaining chlorine is this :—

Exp. 116.—Place in a flask 50 grams of powdered manganese dioxide, and pour upon it 250 c. c. of common hydrochloric acid previously diluted with one-third of its bulk of water; chlorine comes off freely, on heating the mixture.

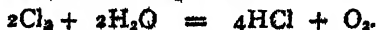
In this case the hydrogen of the acid is wholly converted into water by the oxygen of the manganese oxide; half the chlorine unites with the manganese, while the other half comes off as gas—



Cold water dissolves about twice its bulk of chlorine.

Exp. 117.—Remove the stopper from a bottle of chlorine gas, close the mouth with a glass plate, plunge the mouth of the bottle into water, and remove the plate: a little water will enter. Close the bottle with the plate, and shake the gas and the water together. Again open it under water: more water will enter: and by repeating the agitation and other operations again two or three times, a solution of the gas in water will be obtained.

The solution of chlorine must be kept in the dark. If exposed to a strong light, water is decomposed and oxygen is set free. The hydrogen of the decomposed water combines with chlorine to form hydrochloric acid, which dissolves in the liquid, and this will redden litmus, and not bleach it. The reaction may be thus represented:



Exp. 118.—Fill a litre bottle with a strong solution of chlorine. Fit a sound cork to the neck; pass through the cork a quill tube open at both ends, and bent twice at right angles, so that the tube shall reach nearly to the bottom of the bottle. Place it in direct sunshine: gas will rise into the upper part of the bottle, and will displace the solution, which must be allowed

to flow over into a vessel placed for its reception. If the cork be withdrawn when sufficient gas has been formed, and a lighted match be introduced, it will burn briskly in the liberated oxygen.

This power of decomposing water and of setting oxygen free often renders chlorine an indirect but powerful means of forwarding oxidation.

The solution of chlorine has the smell and taste of the gas. When cooled down to near the freezing point of water, crystals of chlorine hydrate are formed. If these crystals are put into a strong tube, so as nearly to fill it, and the tube be carefully sealed, the crystals will melt when the temperature rises, and yellow oily-looking drops of liquid chlorine will separate, and subside through the water. They exert at 15°C . a pressure equal to about 4 atmospheres.

Chlorine is not inflammable.

Exp. 119.—Plunge a lighted taper into the gas : it burns feebly, with a red smoky flame.

Chlorine combines at once with many elementary substances with great energy.

Exp. 120.—Place a piece of dry phosphorus in a copper deflagrating spoon ; introduce it into a bottle of chlorine gas : the phosphorus takes fire, and burns with a pale greenish flame, while suffocating fumes of phosphoric chloride (PCl_5) are formed.

Exp. 121.—Dip a strip of blotting-paper into oil of turpentine ; plunge it into a jar of chlorine gas : it immediately bursts into flame, whilst a dense black smoke is given off.

In this case the chlorine unites with the hydrogen of the oil of turpentine, and the carbon is separated.

Exp. 122.—Powder some metallic antimony finely in a mortar, and sprinkle a little of it into a jar of chlorine : it takes fire as it falls, giving out fumes of antimonious chloride (SbCl_3), which are very irritating.

Copper leaf, powdered bismuth, and many other metals, when in a sufficiently finely divided state, take fire when introduced into chlorine, forming chlorides by their union with the gas. In all cases where chlorine combines with

another elementary body, the new compound is termed a *chloride*.

This energetic action of chlorine renders it of great value as a disinfectant, for it immediately decomposes all animal effluvia with which it comes into contact, and converts them into new and harmless substances.

Another very important property of chlorine is its bleaching power. Many vegetable and animal colours are attacked, when moist, by chlorine, which removes a portion of their hydrogen, while a corresponding quantity of chlorine takes its place, often forming a substance which has little or no colour. In other cases the chlorine acts by removing hydrogen from water, setting oxygen free, and thus, at the moment of its liberation, decomposes the colouring material.

Exp 123.—Pour a little boiling water upon some chips of log-wood, so as to obtain a deep red liquid. add a little of the solution of chlorine, and the red colour will be discharged.

Common writing-ink, infusions of cochineal, of brazil-wood, of litmus, and of many other colouring matters, will also be bleached by it with facility. Chlorine is very extensively used for bleaching purposes in the manufacture of cotton goods and of paper, as well as in calico printing and in dyeing.

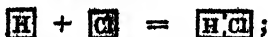
(25) HYDROCHLORIC ACID : *Symb.* HCl; *Atomic Wt.* 36.5; *Atomic and Mol. Vol.* , *Sp. Gr.* 1.2474, *Relative Wt.* 18.25.

Hydrogen and chlorine have a very powerful attraction for each other. If equal measures of the two gases be mixed together, and exposed to direct sunlight, or other strong light, such as that of burning magnesium, they combine instantly, with a powerful explosion, in diffused daylight they gradually unite, but the mixture may be preserved unaltered if kept in the dark.

Exp 124.—Wrap up a soda-water bottle in a towel; fill it with water, and invert it in the pneumatic trough. Introduce a

glass funnel into the neck, and, having filled a jar of 100 c. c. capacity with chlorine, decant the gas into the bottle. Fill the same jar with hydrogen, and decant that into the same bottle; withdraw the funnel, close the neck with the palm of the hand, lift the bottle out of the water-bath, give it a shake to mix the gases, and apply a lighted match. A sharp explosion immediately follows, and gaseous hydrochloric acid is formed.

Equal measures of hydrogen and chlorine unite in this way, and the gas produced occupies the same bulk that its components did when separate—



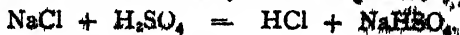
but owing to the action of chlorine on mercury, and its solubility in water, it is not easy to make this experiment with accuracy.

Hydrochloric acid gas is transparent and colourless; it has a pungent irritating smell, and an intensely acid taste; it also makes the eyes smart. This acid is not inflammable, and it will not allow a candle to burn in it. It is also injurious to vegetation. It is heavier than air, and is very soluble in water, producing a powerfully acid solution. By a very strong pressure, the gas may be reduced to a liquid, which has never been frozen.

Exp. 125.—Melt 200 or 300 grams of common salt in a clay crucible at a good red heat, and pour out the salt when melted upon a dry stone slab, or into a clean iron shovel. When cold, break up the mass into pieces of the size of a pea, and preserve them in a dry bottle. Introduce 50 grams of the chloride* into a flask provided with a cork and bent tube, having poured over it about twice its weight of oil of vitriol. Hydrochloric acid gas comes off, even in the cold, but it is extracted still more abundantly when heated. Collect the gas in dry bottles by downward displacement. It may easily be ascertained when the bottle is full, as a lighted taper will be extinguished if introduced only into its neck.

* Other chlorides—such as chloride of potassium, ammonium, or calcium—might be used; but common salt, as the cheapest, is always preferred for preparing hydrochloric acid.

This gas emits copious whitish fumes as it escapes into the air, owing to its combining with the moisture of the atmosphere, and condensing it into the form of liquid globules, which again slowly evaporate. The reaction which accompanies its formation may be thus represented :



Exp. 126.—Fill a flask with the gas by displacement, close the neck with the thumb, and immerse it in a basin containing infusion of litmus ; on removing the thumb, the blue liquid will rush into the flask, and will become red.

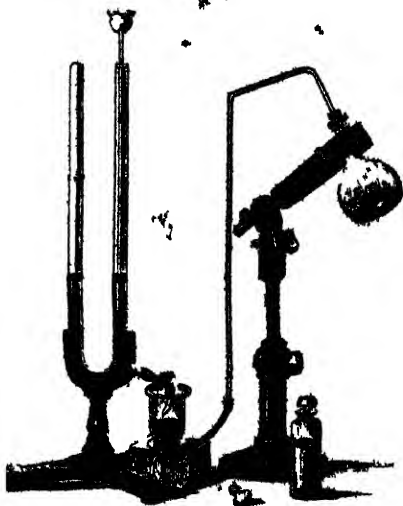
The presence of hydrogen and chlorine in the acid gas may be proved analytically as follows :—

Exp. 127.—Heat two or three globules of sodium of the size of a pea in a copper spoon in the flame of a spirit lamp till they begin to burn ; then plunge them into a jar of hydrochloric acid gas. The sodium will take fire and burn.

Fig. 59.

In this experiment the hydrochloric acid is decomposed, the sodium uniting with the chlorine to form common salt, while the hydrogen is set free.

Hydrochloric acid contains half its bulk of hydrogen, as may be shown by an exact analysis of the gas by means of a so-



lution of sodium in mercury, which may be effected in the following manner :—Fill a bent tube (Fig. 59) with mercury, slip a piece of flexible tube over the end of a quill tube

connected with a glass flask from which hydrochloric acid gas is being disengaged, and, having passed the flexible tube round the bend into the closed limb of the U tube, allow hydrochloric acid to pass until the closed limb is two-thirds full. The displaced mercury must be allowed to escape at the quill tube, on which the screw-tap is relaxed; then withdraw the flask and tube, and close the screw-tap on the U tube. Pour in mercury until it stands at the same level in both limbs. Now slip a small elastic ring over the sealed tube, so as to mark the height at which the mercury stands; fill up the open limb with an amalgam of sodium, prepared by dissolving 6 or 8 pieces of sodium the size of a pea in 30 c. c. of mercury. Close the tube with a good cork. Transfer the gas into the limb containing the amalgam, and agitate it briskly: sodic chloride will be formed. Retransfer the gas to the closed limb, allow mercury to run off till it stands at the same level in both limbs: it will be found that the gas has been reduced to half its original bulk, and that which is left is hydrogen, for it will burn on the approach of a light.

Exp. 128.—Fill a dry bottle with hydrochloric acid gas, and close the mouth with a glass plate. Withdraw the stopper from a bottle of ammoniacal gas of the same size; invert the jar of hydrochloric acid over the one containing the ammonia, and remove the glass plate. The two invisible gases will suddenly combine, a dense white cloud will be formed, and a solid salt (sal ammoniac, or ammonium chloride) will be produced.

Equal bulks of the two gases unite and condense each other, $\text{HCl} + \text{H}_3\text{N}$ becoming H_4NCl . The group H_4N has never been obtained in a separate form; but many chemists regard it as a compound metal, called *ammonium*, which combines with chlorine, and completely neutralises its activity, just as sodium does in common salt, NaCl resembling $(\text{H}_4\text{N})\text{Cl}$ in many important points.

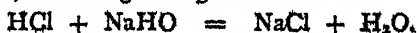
A solution of hydrochloric acid in water forms an important and powerful chemical agent. It is frequently spoken of as *mariac acid*, from the word *maria*, brine. The

common commercial acid has often a yellow colour, owing to the presence of a little iron. It is a fuming liquid, of sp gr about 1.17, and contains about a third of its weight of the gas. A solution of hydrochloric acid may readily be prepared by connecting a flask charged with a mixture of fused salt and oil of vitriol with an apparatus similar to that employed for obtaining a solution of ammonia (Fig. 57). This acid dissolves those metals which decompose steam when passed over them at a red heat, such as zinc, iron, nickel, and tin, with escape of hydrogen, while chlorides of the metals are formed.



Exp 129—Dilute a little hydrochloric acid with 6 or 8 times its bulk of water, and add caustic soda cautiously, until the liquid is exactly neutral, and neither reddens blue litmus nor restores the blue to red litmus paper. Pour the liquid into a basin, and evaporate it slowly; crystals of common salt will be deposited in cubes.

In this case the whole of the hydrogen of the acid, in combination with oxygen derived from the soda, will pass off as water, the change being as follows—



Exp 130—Pass a piece of quicklime into a tube filled with hydrochloric acid gas standing over mercury; the gas will be quickly absorbed.

The change is the following:—



calcic chloride and water being formed.

Most of the chlorides are soluble in water; and when a solution of a strong base, such as potash, is added to the solution of a chloride of one of the metals which forms an insoluble oxide, the oxide, and not the metal, is precipitated.

Exp. 131.—Add a solution of caustic potash to a diluted solution of cupric chloride.

In this case hydrated cupric oxide is thrown down, of a pale blue colour—



If a more complex oxide be acted on, a corresponding chloride is formed, if the formation of such a compound be possible. For instance, ferric oxide may be dissolved by hydrochloric acid, and the change is thus shown—



But if there be no chloride corresponding to the oxide, part of the chlorine escapes, while a chloride of simpler composition is formed, as in the common process of obtaining chlorine gas, by acting on manganese dioxide, to which there is no corresponding chloride, $\text{MnO}_2 + 4\text{HCl}$ becoming $\text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$.

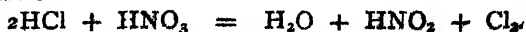
Hydrochloric acid and the chlorides are easily distinguished when present in solution by the following tests:—

Exp. 132.—Dissolve 0.2 gram of sodic chloride in 100 c. c. of water, and divide it into two portions. (1) To one of these add a few drops of a solution of argentic nitrate: an abundant white cloud of argentic chloride (AgCl) will be formed. Divide this milky liquid into two portions. To one of them add a few drops of nitric acid: no change will be perceptible. To the other add a few drops of ammonia solution: the liquid will become clear, since ammonia dissolves argentic chloride readily. (2) To another portion of the sodic chloride solution add a few drops of a solution of mercurous nitrate: a white precipitate of calomel will appear. Divide this turbid solution into two portions. Add a few drops of nitric acid to one: no change will occur. To the other add ammonia: the precipitate will become black.

Exp. 133.—Boil hydrochloric acid in a test-tube with fragments of gold leaf: they will not be dissolved. Now add a drop or two of nitric acid: a yellow solution of auric chloride (AuCl_3) will be quickly formed.

Scraps of platinum are not dissolved by hydrochloric acid, but they enter slowly into solution if nitric acid be added and the mixture be warmed. This mixture of hydrochloric with nitric acid is often called *aqua regia* (royal water),

from its power of dissolving gold, which was regarded by the alchemists as the king of metals. This mixture of acids is often useful for dissolving ores which resist either acid singly. It owes its activity to the chlorine which is set free. In using the liquid, it should be only gently warmed, because if boiled the chlorine is quickly expelled to waste. Some oxychlorides of nitrogen are formed at the same time, and pass off in red vapours; but the chlorine is really the active substance—



If the hydrochloric acid be used in excess, chlorides only remain in the liquid, the whole of the nitric acid being decomposed and going off with the gases.

(26) *Oxides of Chlorine.*—Chlorine does not combine directly with oxygen, but it forms with it three gaseous compounds, all of which have a red or yellow colour, a peculiar irritating odour, a corrosive action, and are all so unstable that they are easily decomposed by heat, and explode with violence. These gases are:

Hypochlorous anhydride	.	.	.	Cl_2O
Chlorous anhydride	.	.	.	Cl_2O_2
Chloric oxide	.	.	.	ClO_2

The first two, when acted on by water, furnish acids; and, in addition, two other acids containing chlorine and oxygen are known. These acids form a regular series, in which the oxygen increases step by step as follows:

Hypochlorous acid	.	.	.	HClO
Chlorous acid	.	.	.	HClO_2
Chloric acid	.	.	.	HClO_3
Perchloric acid	.	.	.	HClO_4

All these acids are very unstable, and they are seldom prepared. Some of their salts, particularly the hypochlorites and chlorates, are important.

Some of these salts are formed by acting upon a strong base with chlorine; but the result varies according to the temperature employed.

but the chlorite is decomposed, as fast as it is formed, into oxygen gas and potassic chloride—



and the chloride, which is very soluble, is easily separated from the sparingly soluble potassic perchlorate. If the perchlorate be heated still more strongly, it in turn is decomposed into oxygen gas and potassic chloride—



(27) 2. BROMINE; *Symb.* Br; *Atom. Wt.* 80; *Atom. Vol.* \square ; *Mol. Wt.* (Br_2) 160; *Mol. Vol.* \square ; *Rel. Wt.* 80; *Sp. gr. of vapour*, 5.54; *of liquid* at 0°C . 3.187; *Boils* at 63°C .; *Freezes* at -12.5° .

Bromine is the only element except mercury which is liquid at ordinary temperatures. It is of a deep red colour, and gives off abundant dark red vapours, which have a very irritating effect upon the eyes and the back of the throat, with a peculiar disagreeable odour, whence its name is derived. It is about three times as heavy as water, and is but sparingly soluble in it, but freely so in alcohol and ether. Its chemical properties are similar to those of chlorine, but less active. It forms a gaseous compound with hydrogen, the hydrobromic acid ($\text{HBr} = 81$; *Sp. Gr.* 2.731; *Rel. Wt.* 42.5), which fumes in air and is extremely soluble in water; it is powerfully acid, and much resembles hydrochloric acid. It may be obtained by decomposing potassic bromide with phosphoric acid. Bromine also forms acids in which oxygen is present; but only two of them—the bromic (HBrO_3), corresponding to the chloric, and perbromic (HBrO_4), corresponding to the perchloric—have been examined carefully.

Bromine is contained in sea water, as magnesian bromide (MgBr_2), in quantity varying from 4 to 14 mgrams. per litre.

Sea water is concentrated in large quantities for the sake of its common salt and potassic and magnesian salts; and when these have been separated by crystallisation, the mother

liquor, or *bittern*, is treated for the bromine. Many strong brine springs, such as those of Kreuznach and Kissingen, also contain small quantities of the bromides. The bittern is made to yield its bromine by transmitting into it a current of chlorine gas, avoiding an excess of it. All the bromides of the metals are decomposed by chlorine, which has a more powerful attraction for the metals than bromine has. The liquid acquires a beautiful golden yellow colour, due to the liberated bromine, $\text{MgBr}_2 + \text{Cl}_2$ becoming $\text{MgCl}_2 + \text{Br}_2$. This yellow liquid is then mixed with ether and shaken up with it. The ether dissolves the bromine; and if the mixture be placed in a glass globe, provided with a stopper at top and a glass stop-cock at bottom, the ether rises in a yellow layer to the surface, and the mother liquor is easily drawn off from below. The ethereal solution is then shaken up with a solution of caustic potash, by which the yellow colour is immediately destroyed: potassic bromide and bromate are formed, and become dissolved in the water, while the ether rises to the surface, and may again be used in a similar manner with fresh portions of bittern. The action of potash upon bromine resembles that which it exerts upon chlorine, $3\text{Br}_2 + 6\text{KHO}$ yielding $\text{KBrO}_3 + 5\text{KBr} + 3\text{H}_2\text{O}$. When the solution of potash has become neutralised by the action of repeated charges of bromine, the liquid is evaporated to dryness, mixed with a little charcoal, and gently heated, to remove the oxygen from the bromate; after which the residue, consisting of bromide and the excess of charcoal, is mixed with manganese dioxide and sulphuric acid in a retort. On applying heat, red vapours of bromine pass over—

$2\text{KBr} + \text{MnO}_2 + 3\text{H}_2\text{SO}_4 = 2\text{KHSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Br}_2$.
The reaction resembles that by which chlorine is obtained.

Exp. 141.—Dissolve 2 or 3 decigrams of potassic bromide in 20 c. c. of water. Mix the solution in a long and wide test-tube, with 5 c. c. of solution of chlorine, and add 5 c. c. of ether. Agitate the mixture: a yellow solution of bromine in ether will rise to the surface. Decant this ethereal solution into another

tube, and shake it with an equal bulk of a solution of caustic potash. The yellow colour will disappear, and the ether will rise to the top, and form a colourless layer.

Bromine combines directly with phosphorus, and with many of the metals. The compound formed by the union of bromine with any other element is called a *bromide*. Argentic bromide is a substance of importance to the photographer.

Exp. 142.—Add a little of a solution of argentic nitrate to a weak solution of potassic bromide: a white precipitate is formed. Divide the liquid with the precipitate into three portions. To one of them add a little nitric acid, to another a few drops of a solution of ammonia: no solution occurs in either case. To the third add a little of a solution of sodic hyposulphite: the liquid becomes clear, a double hyposulphite of silver and sodium being formed.

The bromides also form a white precipitate of mercurous bromide (HgBr) with a solution of mercurous nitrate; and a white precipitate with lead nitrate, consisting of lead bromide (PbBr_2). Chlorine water decomposes both, setting bromine free, and forming a chloride of mercury or of lead.

(28) 3. IODINE: *Symb.* I; *Atomic Wt.* 127; *Atomic vol. of vapour* \square ; *Mol. Vol.* \square (I_2); *Rel. Wt.* 127; *Sp. gr. of vapour*, 8.716; *of solid*, 4.947; *Melting Pt.* 107°C. ; *Boiling Pt.* 175°C.

Iodine is a solid, which crystallises in bluish-black scales, resembling plumbago in lustre. It is volatile at ordinary temperatures, and emits a feeble smell, resembling that of chlorine, and sublim^s* slowly in the bottles in which it is kept, and is deposited in crystals on the sides. When heated to a little beyond 100°C. it melts, and at a higher temperature gives off dense vapours, of a rich violet hue, whence it derives its name.

* A body which rises in vapour and condenses in the solid form is said to *sublime*, in opposition to one which condenses in the liquid form, when it is said to *distil*.

Exp. 143.—Place about 0.2 gram of iodine in a flask; warm it over a lamp. The iodine will melt to a brown liquid; and if the flask be heated gradually and uniformly, beautiful violet vapours will fill it. When allowed to cool, its interior will be coated over with small crystals of sublimed iodine.

Iodine stains the skin and most organic substances brown, and gradually corrodes them. Water dissolves it but sparingly, alcohol and ether freely; solutions of the iodides in water also dissolve it.

Exp. 144.—Take four test-tubes, and place about a decigram of iodine in each. Pour into the first 2 c.c. of water, into the second the same quantity of alcohol, into the third the same quantity of ether, to the fourth add 0.2 gram of potassic iodide, and then a little water. A pale-yellow liquid will be formed in the first tube, and scarcely any iodine will be dissolved, whilst the iodine will be dissolved in each of the other tubes, and will form a deep-brown solution. Mix the solution in alcohol with twice its bulk of water: most of the iodine will separate in scales, as it is not soluble in water, and the water immediately separates the alcohol from the iodine. Mix the solution in the fourth tube with water: no precipitation will occur, because the potassic iodide retains the iodide dissolved.

Exp. 145.—Place about 0.3 gram of iodine in a test-tube with a few drops of water, and add about 0.1 gram of iron filings: a green solution of ferrous iodide will be formed.

Exp. 146.—Let zinc filings be substituted for iron, and a colourless solution of zinc iodide will be obtained.

When an element combines with iodine, the compound is known as an *iodide*.

All the iodides of the metals are readily decomposed by chlorine, and even by bromine, while the iodine is set free. This is taken advantage of in testing for iodine. The most delicate test for free iodine is the intense blue colour which it yields with cold starch paste.

Exp. 147.—Mix 1 gram of white starch with 10 grams of water, and pour it slowly into 40 or 50 grams of boiling water; boil for a minute, and allow it to cool. Mix a little of this mucilage with water, and add one or two drops of any of the

solutions of iodine prepared as above directed : the intense blue iodide of starch is immediately formed.

Exp. 148.—Mix one or two drops of a solution of potassic iodide with a little of the diluted starch mucilage : no change of colour will occur. Add a single drop of chlorine water to the mixture : an immediate coloration will occur, owing to the combination of the chlorine with the potassium, while iodine is set free, and acts upon the starch. Add a little more chlorine water : the colour disappears, owing to the formation of chlorine iodide, which is without action on starch.

A solution of bleaching powder may be used instead of chlorine water, or, still better, a solution of potassic nitrite, to which a drop or two of acetic acid has been added. An excess of nitrite does not interfere with the blue colour.

Exp. 149.—Heat the blue solution of starch iodide to boiling : the colour fades, and often quite disappears. Cool the solution, and the blue colour returns.

The cause of this change of colour is not known.

Other tests for the iodides, though of less delicacy, are the following : A solution of lead salt, when mixed with a soluble iodide, gives beautiful silky yellow scales of lead iodide (PbI_2). A silver salt, such as argentic nitrate, gives a pale buff-coloured argentic iodide (AgI), nearly insoluble in ammonia. Mercuric chloride gives a yellow precipitate of mercuric iodide (HgI_2), quickly passing into scarlet.

Exp. 150.—Divide the last named solution with its precipitate into two portions. To one portion add a little more of the mercurial solution : the precipitate will be redissolved. To the other portion add an excess of potassic iodide : this also, will redissolve the precipitate.

Hence it will be seen that an excess of either salt must be avoided when testing for iodides or for mercury.

Iodine is contained in minute proportion in sea water, from which it is extracted by the sea-weeds during their growth, and stored in their tissues. In order to obtain the iodine, the weeds are first dried in the sun, and then burned,

at a low temperature, in shallow pits on the shore; the ashes forming what is called *kelp*. The iodine is present in this ash as sodic iodide. The soluble matters are washed out of the ash, and the liquor is evaporated, to allow most of the salts of potassium and sodium to crystallise out. Sulphuric acid is then added to the mother liquor; and after the effervescence due to the escape of carbonic anhydride and gaseous compounds of sulphur is over, the acid liquor is run off into stills, mixed with powdered manganese dioxide, and distilled, at a gentle heat—



The decomposition which occurs resembles that which attends the liberation of chlorine or of bromine, as already described. Violet vapours of iodine come off, and are condensed in a series of globular receivers. The crude iodine thus obtained is purified by a second sublimation.

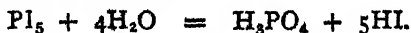
HYDRIODIC ACID: *Symb.* HI; *Atom. and Mol. Wt.* 128; *Mol. Vol.* x; *Sp. Gr.* 4.443; *Rel. Wt.* 64.

Exp. 151.—Dry a piece of phosphorus of the size of a split pen, and place it on a saucer. Then let a few crystals of iodine fall upon it. In a few moments the two bodies will unite, and so much heat will be given out that the phosphorus will take fire.

In this experiment one portion of phosphorus burns in the air, while another portion unites with the iodine to form phosphorous iodide (PI_3).

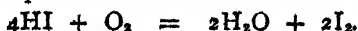
Exp. 152.—Place in a small retort 2 grams of iodine, 1 c. c. of water, and then add 0.1 gram of phosphorus.

In this case phosphorous iodide is also formed as before, but it is now decomposed by the water, and phosphoric and hydriodic acids are formed—



On heating the mixture gently, hydriodic acid gas will escape, and may be collected by downward displacement in a wide test-tube.

Hydriodic acid gas extinguishes a light, and does not itself burn; it is more than four times as heavy as atmospheric air; it is colourless, but fumes strongly when it escapes, owing to its condensing the moisture present in the air. It is very soluble in water, with which it forms an intensely acid liquid. Chlorine immediately decomposes it, and sets iodine at liberty. Its solution in water, if exposed to the air, gradually absorbs oxygen; the hydrogen unites with the oxygen, and the liquid becomes brown from liberated iodine—



Iodine forms a white oxide, iodic anhydride (I_2O_5), corresponding to nitric anhydride. There are also two acids of iodine containing oxygen, viz. the iodic (HIO_3) and the periodic (HIO_4); but they are not of practical importance

(29) 4. FLUORINE: *Symb.* F; *Atom. Wt.* 19.

Many unsuccessful attempts have been made to obtain fluorine in an isolated state, but its chemical activity is so great that it combines with the metal or glass with which it is in contact at the moment that it is set free; so that no satisfactory knowledge of free fluorine has yet been obtained. Its compounds with other elements are termed *fluorides*.

The most important and abundant natural compound of fluorine is calcic fluoride or fluor spar (CaF_2), a mineral which is insoluble in water, colourless when pure, but more frequently met with in beautifully-veined blue or green masses, which, when crystallised, occur in cubes, or some forms derived from the cube.

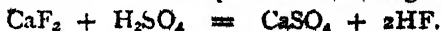
Cryolite, a fluoride of aluminum and sodium ($3\text{NaF}, \text{AlF}_3$), is also found abundantly in Greenland.

No oxides or oxygen acids of fluorine are known; but when combined with hydrogen, it furnishes an intensely corrosive acid, the *hydrofluoric* (HF), which immediately attacks glass, so that it cannot be prepared or preserved in glass vessels. Its fumes are dangerously irritating, and great care must be taken to avoid inhaling them. The acid

is freely soluble in water, and is often prepared in a diluted form for etching on glass, as, for instance, in engraving thermometer scales, and for similar purposes. This diluted acid may be preserved in silver or leaden bottles, or, as is more usual, in vessels made of gutta percha.

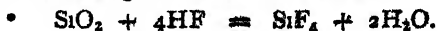
Exp. 153.—Powder a gram of fluor spar finely, and place it in a small shallow leaden cup, 6 or 8 centim. in diameter, and pour over it 2 or 3 grams of oil of vitrol; then place over the leaden cup a plate of glass large enough to cover it, prepared in the following manner:—Cover one side of the glass with a thin uniform layer of beeswax, which may be done by warming the glass and rubbing it over with the wax. When the glass is cold, trace a few characters with the point of a knife through the wax, so as to expose the glass beneath. Place the glass with the waxed surface downwards over the leaden dish, and warm it gently, taking care not to melt the wax. Vapours of hydrofluoric acid will be given off, which in a few minutes will corrode the glass where it is exposed, but will not attack the wax.

The acid acts on the fluor spar in the following manner:—



On cleaning off the beeswax with a little oil of turpentine, the design will be found more or less distinctly etched upon the glass plate. A very small quantity of fluorine compound may be detected in a mixture by proceeding carefully in the same manner. In the enamel of the teeth, and often in fossil bones, fluorine exists in quantity sufficient to be easily detected in this way.

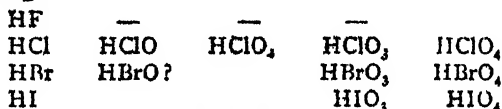
The hydrofluoric acid attacks the silica of the glass, furnishing water and gaseous silicic fluoride—



This action of hydrofluoric acid renders it a valuable agent in the analysis of the silicates in many cases where the ordinary acids do not decompose them. Argentic fluoride is soluble, so that the fluorides give no precipitate with argentic nitrate. The acid unites with potassic fluoride, and forms a crystalline compound (KF, HF), from which the anhydrous hydrofluoric acid has been obtained. (*See Appendix.*)

All the halogens—fluorine, chlorine, bromine, and iodine—are regarded as monads, since they are characterised by forming a very soluble powerfully acid gas when united with hydrogen, such as the hydrofluoric, hydrochloric, hydrobromic, and hydriodic. No condensation accompanies the combination, for analysis shows that in each case the acid contains half its bulk of hydrogen, the hydrogen being united with its own volume of the halogen, the gaseous acid occupying the same bulk as its component gases of vapours did in their separate form.

With the exception of fluorine, each of these elements emits a coloured vapour: each, though incombustible in oxygen, yet forms acids with it, the series known being the following:—



In comparing the halogens with each other, the chemical activity of fluorine, which has the smallest atomic weight, is the most powerful; next in the order in activity is chlorine, then bromine, and, lastly, iodine, the atomic weight increasing as the chemical energy declines. Chlorine is gaseous, bromine liquid, and iodine solid. The specific gravity, the fusing point, and the boiling point, rise as the atomic weight increases. The halogens combine energetically with the metals, and, when united with the same metal, furnish compounds which are *isomorphous*; that is to say, they all crystallise in the same form—potassic fluoride, chloride, bromide, and iodide, for example, all crystallise in cubes.

CHAPTER VII.

SULPHUR GROUP.

1. SULPHUR. 2. SELENIUM. 3. TELLURIUM.

(30) 1. SULPHUR: *Symb.* S; *Atom. Wt.* 32; *Melting Pt.* 115°; *Boiling Pt.* 446° C.

Sulphur, or *brimstone*, has been known from time immemorial, as it is an element found uncombined in considerable quantities in volcanic districts. It is also found in combination with many of the metals; for instance, when united with iron it forms the yellow brassy-looking mineral known as iron pyrites; with lead it furnishes galena, the principal ore of lead; and with zinc it gives the brown mineral called blende. In combination with oxygen, it is found forming salts with other metals, known as sulphates, among which those of calcium, magnesium, and barium are of most frequent occurrence. Sulphur also occurs in combination in white of egg, in muscle, and some other animal products.

Sulphur is a yellow brittle solid, which is not soluble in water, but is soluble in carbon disulphide, oil of turpentine, and in benzol, as well as to a slight extent in hot alcohol. It is highly inflammable, and burns with a blue flame, emitting pungent suffocating vapours of sulphurous anhydride. When heated to 115° C. it melts, forming a transparent yellow liquid, which undergoes a series of curious changes by the continued application of heat.

Exp. 154.—Place a few grams of sulphur in a wide test-tube, and apply the heat of a lamp cautiously. The sulphur melts and forms a pale yellow liquid, which flows easily. Pour part of the melted mass into cold water: a yellow brittle solid is formed. Heat the portion still left in the tube more strongly: it gradually deepens in colour, and becomes thick, assuming a treacly appearance. On heating the sulphur still higher, it again becomes somewhat more fluid. Pour it now in a thin stream into cold water: the sulphur forms into tough, elastic, semi-transparent strings.

The colour of these cooled threads varies from a pale amber to a deep brown, becoming darker in proportion as the heat applied is greater. If kept for a day or two, this elastic sulphur gradually becomes hard, opaque, and brittle.

Sulphur may easily be obtained in crystals.

Exp. 155.—Melt from a quarter to half a kilogram of sulphur in an earthen pipkin at a low and carefully applied heat. When completely melted, set it aside to cool slowly. Allow it to stand for a short time after it has become solid over the surface; then, with a hot wire, pierce two holes through the crust near the edge on opposite sides, and pour out the still liquid portion.

When the mass is cold, remove the solid crust carefully, and the interior will be found to be lined with transparent honey-yellow needles, which, when scratched, or even when left to themselves for a few hours, gradually become opaque. The crystals thus obtained belong to the class known as the oblique prismatic.

Sulphur may also be obtained in crystals of a different form, the octahedron with a rhombic base. Native sulphur assumes this shape; and it may be obtained by dissolving sulphur in carbon disulphide, and allowing the solution to evaporate spontaneously. This form has a sp. gr. of 2.05, while the crystals obtained by fusion (*Exp. 155*) are less dense, being only of sp. gr. 1.98. They also have different fusing points, the octahedral sulphur fusing at 115° , and the prismatic requiring a temperature at 120° C. for its fusion.

Bodies which, like sulphur, can be obtained in forms which belong to two distinct classes of crystals are said to be *dimorphous*.

Sulphur also offers a good instance of allotropy. In these two varieties of crystalline form, and in the elastic threads, or viscous state obtained by sudden cooling from a high temperature, we have three different modifications of the same element. A fourth may also be procured by placing in carbon disulphide the hard mass furnished by keeping the viscous sulphur till it becomes solid. The carbon disulphide

dissolves all that can be removed from the mass, and a grey amorphous (or non-crystalline) powder is left; this differs from the crystalline varieties in its singular insolubility in carbon disulphide, which dissolves both the crystalline forms readily.

All these different varieties of sulphur may be distilled by the application of sufficient heat, provided air be excluded, otherwise they would take fire. The distilled sulphur thus obtained exhibits no difference in properties, whichever allotropic modification may have been used.

Exp. 156.—Place a few pieces of sulphur in a Florence flask. Cut off the neck of a second flask, so as to enable the neck of the first flask to pass into the second, as shown in Fig. 60. Heat the flask containing the sulphur, covering the upper surface with a cone of thin sheet iron, to keep it hot. The sulphur first melts, then boils, and ultimately distils over into the second flask.

The vapour of sulphur, at temperatures of about 500° , is 96 times as heavy as that of an equal volume of hydrogen at the same temperature; but if the sulphur vapour be heated to 1000° C. it becomes expanded, until its density is only 32 times that of hydrogen at the same temperature and pressure.

Selenium and tellurium show the same curious exceptional effect of heat upon their vapours.

The compounds which sulphur forms with any of the other elements are termed *sulphides*, or sometimes *sulphurats*.

Fig. 60.



Advantage is taken of the volatility of sulphur to purify it from earthy matters. It is usually distilled roughly on the spot where it is found, and afterwards purified by a second more careful distillation. The roll sulphur of commerce is obtained by pouring the melted sulphur into cylindrical wooden moulds, in which it is allowed to cool. *Flowers of sulphur*, as they are called, occur in the form of a harsh yellow crystalline powder, which is procured by distilling sulphur slowly into a large brickwork chamber, where the fumes become condensed in this form. If distilled more quickly, the brickwork becomes hot, and then the sulphur melts and runs down the sides, forming a solid mass as it cools.

Sulphur, from its ready inflammability, is used in the preparation of matches. Large quantities are also employed in the manufacture of gunpowder; but its principal consumption is in the production of sulphuric acid.

Sulphur combines directly with many of the metals, and gives out much heat in the process.

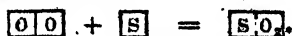
Exp. 157.—Mix 3 or 4 grams of copper filings with half their weight of flowers of sulphur, and heat them in a large test-tube. At a temperature a little above the melting-point of sulphur the two bodies will begin to unite, and a bright glow will spread through the mass. When the tube is cold, break it and examine the product. A substance in no way resembling copper or sulphur will be found: it consists of the sulphide of the metal.

Two compounds of sulphur with oxygen are known, sulphurous anhydride (SO_2) and sulphuric anhydride (SO_3), both of which furnish important acids when combined with water. There are also other acids of sulphur containing oxygen: these are known as the *polythionic series*, in reference to the multiple proportion in which sulphur (*θειον*) enters into their formation. It will be sufficient merely to give their formulae. The series of oxygen-sulphur acids is as follows—

Hydrosulphurous acid	H_2SO_2	Dithionic acid	$\text{H}_2\text{S}_2\text{O}_6$
Sulphurous acid	H_2SO_3	Trithionic acid	$\text{H}_2\text{S}_3\text{O}_6$
Sulphuric acid	H_2SO_4	Tetrathionic acid	$\text{H}_2\text{S}_4\text{O}_6$
Hyposulphurous acid	$\text{H}_2\text{S}_2\text{O}_3$	Pentathionic acid	$\text{H}_2\text{S}_5\text{O}_6$

(31) SULPHUROUS ANHYDRIDE (or *Sulphur Dioxide*):
Symb. SO_2 ; *Atom. and Mol. Wt.* 64; *Atom. and Mol. Vol.* $\boxed{\text{O O}}$; *Spec. grav. of gas*, 2.247; *Rel. Wt.* 32; *Boiling Pt.* -10°C. ; *Melting Pt.* -76° .

Sulphur burns in oxygen with a lilac flame, and produces a permanent gas, which, after it has again become cool, occupies the same bulk as the original oxygen, but it has become doubled in density. Two volumes of oxygen unite with one volume of sulphur vapour, the three volumes becoming condensed into two—

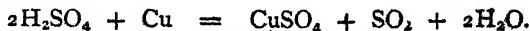


The gas so produced has a pungent and suffocating odour; in a concentrated form it cannot be breathed, but in a diluted state it excites the symptoms of a common cold. It is transparent and colourless, is not inflammable, and immediately extinguishes the flame of burning bodies. Water dissolves more than 40 times its bulk of the gas, and furnishes sulphurous acid—



The solution has the smell and taste of the gas, which readily escapes from the water when heated.

Sulphurous anhydride is usually obtained by heating sulphuric acid in contact with a metal, such as copper: sulphurous anhydride comes off, while water and cupric sulphate is formed—



Exp. 158.—Place about 5 grams of copper clippings in a flask provided with a cork and bent tube, and pour upon it 30 c. c. of oil of vitriol. Heat the mixture strongly, and collect, by downward displacement, 2 or 3 jars of the gas that is given off. Test one jar with a piece of blue litmus paper: the blue will immediately be reddened. Plunge a lighted taper into another jar: it will be extinguished.

Exp. 159.—Suspend a bunch of violets or a rose in a jar of the gas: they will be bleached completely. Throw the flowers into a very weak solution of ammonia: the colour will first be restored, and will then be changed to green by the alkali.

The bleaching action of this gas differs from that of chlorine in not destroying the colour, for this is again restored by the action of an alkali or a stronger acid.

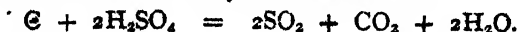
Flannel, sponge, silken goods, isinglass, and many articles which would be injured by chlorine, are bleached by suspending them, in a damp state, in a closed chamber, and then exposing them to the fumes of burning sulphur. (*See Appendix.*)

Sulphurous anhydride is useful as a fumigation for destroying infection. By its action, meat is also preserved from putrefying for a while; and it is frequently employed to check fermentation in cider and home-made wines, for which purpose a little sulphur is burnt in the cask before filling it with the liquor.

There are various other modes of obtaining the gas. One of these consists in heating a mixture of powdered black manganese oxide with about its own weight of sulphur; half the sulphur combines with the oxygen, the other half with the manganese—



If charcoal is boiled with sulphuric acid, a mixture of sulphurous and carbonic anhydrides are evolved—



In the manufacture of sulphuric acid, sulphurous anhydride is supplied simply by burning sulphur or iron pyrites in a current of air. In this way it is obtained mixed with a large bulk of nitrogen. Sulphurous anhydride is also emitted largely from the craters of volcanoes.

When dissolved in water, the gas furnishes sulphurous acid, and this acid furnishes the salts known as *sulphites*. The sulphites of the alkalis may be obtained by passing the gas into a solution of potash or soda. It forms two kinds of salts: one of these contains two atoms of the metal, such as the common disodic sulphite ($\text{Na}_2\text{SO}_3, 10\text{H}_2\text{O}$), while the other kind of salt is frequently called a bisulphite, and contains but a single atom of the metal. Hydric potassic sulphite (KHSO_3) is the best example of this class.

The sulphites are easily distinguished by their effervescing when treated with a strong acid, such as the hydrochloric, giving off a colourless gas, with the pungent characteristic odour of sulphurous anhydride.

Exp. 160.—Add a little of a solution of baric chloride to a solution of a sulphite. A white precipitate of baric sulphite (BaSO_3) is formed.

In this case, if the sulphite be free from sulphate, the precipitate will be dissolved on adding a little hydrochloric acid, but the clear liquid will be rendered milky by the addition of chlorine water, which will convert the sulphurous into sulphuric acid, and this will give a white precipitate of baric sulphate, which is insoluble in acids.

The chlorine takes hydrogen from the water, forming hydrochloric acid, and the oxygen which is set free converts the sulphurous into sulphuric acid—

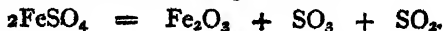


(32) SULPHURIC ACID (*Dihydric Sulphate*): *Symbol*, H_2SO_4 ; *Mol. Wt.* 98, *Sp. grav. of liquid*, 1.846; *Melting Pt.* $10\ 5^\circ \text{C.}$; *Boiling Pt.* 338° .

This is the most important of the acids, and is the basis of our chemical manufactures. The consumption of it annually in this country considerably exceeds 100,000 tons, or one hundred million kilograms.

Exp. 161.—Dry some of the green crystals of ferrous sulphate (the salt formerly called *green vitriol*), and place the dried salt in a test-tube, and heat it nearly to redness. White acid fumes are given off, which condense in oily-looking drops, they are mixed with the pungent vapours of sulphurous anhydride. When all the acid is expelled, a red powder, consisting of ferric oxide, or *colcothar*, as it is called, is left in the tube.

The changes may be thus represented—



From the oily appearance of the product the old name of *oil of vitriol* was derived.

When thus prepared, the distilled liquid consists of a mixture of sulphuric acid with sulphuric anhydride (H_2SO_4 , SO_3). Some sulphuric acid is always formed during the operation, because the ferrous salt cannot in practice be completely freed from water before it is distilled. This water comes away during distillation; and as soon as the anhydride, which distils off also, becomes mixed with water, combination between the two occurs, and sulphuric acid is formed, $\text{SO}_3 + \text{H}_2\text{O}$ becoming H_2SO_4 .

The distillation of dried sulphate of iron has long been conducted on a considerable scale at the town of Nordhausen, in Saxony, where it is made for the purpose of dissolving indigo for the preparation of Saxony blue, and hence the acid so prepared is generally called *Nordhausen Sulphuric Acid*. When such sulphuric acid, holding sulphuric anhydride in solution (H_2SO_4 , SO_3), is heated, the sulphuric anhydride (SO_3) comes off in dense white fumes, which, if immediately shut up in a vessel excluded from the moisture of the air, become converted, as it cools, into a silky-looking white fibrous mass. This substance is not acid, though it immediately becomes so when mixed with water. It combines with water with the evolution of a very high temperature, emitting a hissing sound, like that produced by quenching a red-hot body in water. After the water has thus combined with the anhydride the two are not separated readily by simple heat. If the acid thus obtained be further diluted with water, this additional quantity of water may be removed by evaporation. During this process the boiling point gradually rises till it reaches 338° ; when this point is attained, the acid has become reduced to the state represented by the formula H_2SO_4 , the whole then distils over, and condenses again unaltered.

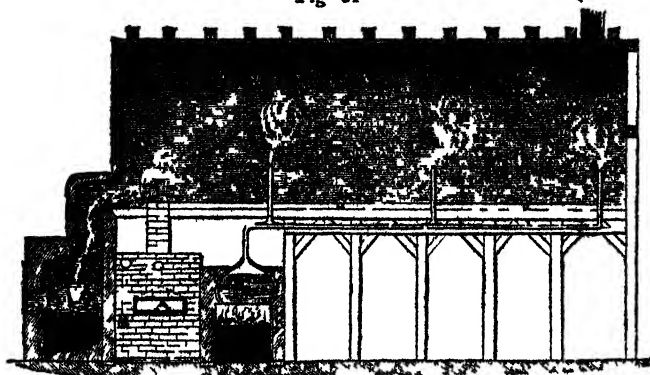
The great bulk of the sulphuric acid required in the arts is, however, obtained by a different process from that just described. When sulphur is burned in dry air or in oxygen, the product is always sulphurous anhydride; it never occurs

as a higher state of oxidation of sulphur, although a higher oxide—namely, the sulphuric anhydride—may be obtained by indirect means. If sulphurous anhydride be mixed with oxygen in the presence of water, and be presented to nitric oxide, or to any other of the higher oxides of nitrogen, the further oxidation of the sulphur may be effected with great rapidity. Moreover, a small proportion of the oxide of nitrogen will effect the combination of an indefinite amount of sulphurous anhydride and oxygen. Nitric oxide (NO) in the presence of oxygen immediately becomes nitrogen peroxide (NO_2), and this, when mixed with sulphurous anhydride and a large quantity of water, furnishes sulphuric acid and nitric oxide. The sulphuric acid remains dissolved in the water, while the nitric oxide, by absorbing oxygen from the air, again becomes nitrogen peroxide; this combines with fresh sulphurous anhydride, which, when acted on by water, becomes sulphuric acid, the nitric oxide being again liberated, to go through the same series of changes with fresh portions of oxygen and sulphurous anhydride as long as any remain in presence of each other uncombined, $\text{NO}_2 + \text{SO}_2 + x \text{H}_2\text{O}$ yielding $\text{NO} + \text{H}_2\text{SO}_4 + x - 1 \text{H}_2\text{O}$.

In making sulphuric acid on a large scale, sulphur or iron pyrites is burned in a current of air in furnaces (A A, Fig. 61). In the stream of heated gas is suspended an iron pot (b), charged with a mixture of sodic nitrate and sulphuric acid. Vapours of nitric acid are thus set free, and these pass on mixed with sulphurous anhydride and excess of atmospheric air. The mingled gases pass into immense chambers (F F), constructed of sheet lead, supported by a framework of timber. A shallow layer of water (d) covers the bottom of the chamber, and the intermixture and chemical action of the gases are further favoured by the injection of jets of steam (e e e), supplied from the boiler (G). (*See Appendix.*) The vapours of nitric acid lose part of their oxygen, and are quickly reduced by the sulphurous acid to the state of nitric oxide, then the changes already described succeed each

other rapidly, leaving ultimately nothing but nitrogen and nitric oxide, which pass off into the atmosphere by a flue (c)

Fig 61



The sulphuric acid which collects at the bottom of the chamber is concentrated by evaporation in shallow leaden pans, till it reaches a sp gr of 1.720, when it forms the *brown* sulphuric acid of commerce. In this state it is largely employed in making manures, and for converting common salt into sodic sulphate. The further concentration must be completed in glass or platinum stills as the leaden pans would melt at the heat required. In these it is further evaporated till the boiling point has risen to 338°C. , and then nothing but the concentrated acid (H_2SO_4) remains. If the application of heat were continued further, the acid would distil over.

The oil of vitriol of commerce is a dense oily looking colourless liquid, without odour, and of sp. gr. 1.842. It is intensely caustic, and chars almost all organic substances, owing to its powerful attraction for moisture. If exposed in a shallow dish to the air for a few days, it increases in weight considerably, by absorbing watery vapour from the air. This property may be made use of for the purpose of drying gases and various other bodies in the laboratory. When

mixed with water, it gives out great heat, so that much care is required in diluting the acid.

Exp. 162.—Pour a little of the strong acid into a test-tube. Place a splinter of wood in it : the wood will be blackened in a few minutes.

Exp. 163.—Pour a cub. centim. of the strong acid into a tube containing 3 or 4 c. c. of water : considerable heat will be felt to attend the mixture. Take a little of this diluted acid, and with a feather dipped into it trace a few letters upon writing-paper. Hold the paper near the fire : the water will evaporate, leaving the acid behind ; this will soon blacken the paper.

It is owing to this kind of action that even a very dilute acid, if left upon linen, will cause it to fall into holes when exposed to the air ; the water evaporates, and the acid, which is not volatile, destroys the fibre.

Tests.—The sulphates, when dissolved in water, may be known by producing a white precipitate when mixed with a solution of a salt of barium, such as baric chloride. This precipitate consists of baric sulphate (BaSO_4). It is not dissolved by nitric acid.

The sulphuric belongs to the class of acids known as dibasic ; that is to say, it contains two atoms of hydrogen, which admit of displacement by a metal ; and, like all acids of this class, it furnishes two sets of salts with metals of which the atom, like the sulphides of the alkali-metals, is chemically equivalent to one atom of hydrogen. Such metals are called monads. In one set of these salts one atom only of hydrogen is displaced by the metal, in the other set both atoms of hydrogen are so displaced. A salt of the first series is often spoken of as an acid salt ; for instance, they may be thus represented, if the formula of sulphuric acid be written as dihydric sulphate (H_2SO_4) ; then—

Hydric potassic sulphate, is HKSO_4 ;

Dipotassic sulphate, or normal sulphate, K_2SO_4 .

But there are cases in which a single atom of a metal, like calcium, displaces both atoms of the hydrogen, and then

but one salt of such metal can be formed. Copper, lead, and barium are metals of this kind. These metals, of which the atom is thus equivalent chemically to two atoms of hydrogen, are called dyads; so that we write—

Baric sulphate	$\text{Ba}''\text{SO}_4$
Calcic sulphate	$\text{Ca}''\text{SO}_4$
Lead sulphate	$\text{Pb}''\text{SO}_4$

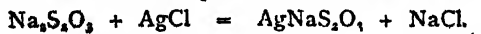
and so on. The two dashes (''), when used, imply that the metal has supplied the place of two atoms of hydrogen.

Lead sulphate is nearly as insoluble as baric sulphate, and strontic sulphate is but little less so. Calcic sulphate is more soluble, though still but slightly so; but most of the other sulphates are freely soluble. The soluble sulphates are often easily formed by dissolving the metal in dilute sulphuric acid; where this cannot be done, the oxide or the carbonate of the metal may be dissolved in the acid—

- (1) $\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2$,
- (2) $\text{CuO} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{H}_2\text{O}$; or
- (3) $\text{MnCO}_3 + \text{H}_2\text{SO}_4 = \text{MnSO}_4 + \text{H}_2\text{O} + \text{CO}_2$.

(33) *Hyposulphites*.—Sodic hyposulphite is a salt which is used extensively by the photographer. This use depends upon the fact that the hyposulphite has the power of dissolving many of the salts of silver which are insoluble in water.

Exp. 164.—Add a solution of sodic hyposulphite to some freshly precipitated argentic chloride (p. 276); the latter will be completely dissolved owing to the formation, by double decomposition, of argentic sodic hyposulphite readily soluble in water—



Argentic bromide and argentic iodide may also be dissolved by the hyposulphite, though not so readily.

When a photograph is washed in water, the excess or soluble argentic nitrate is washed out, but the chloride of iodide remains in the paper. If now this be plunged into a solution of sodic hyposulphite, the portion of unaltered insoluble silver salt becomes dissolved in the liquid, while the

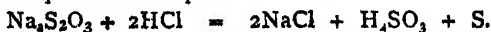
part which has been blackened by light is unacted on. If the picture is then thoroughly washed in pure water it is *fixed*; that is, it becomes no longer liable to change on exposure to light.

There are several ways of preparing sodic hyposulphite. One of the simplest consists in digesting a solution of sodic sulphite upon flowers of sulphur—



A colourless solution is obtained, from which, on evaporation, large colourless striated crystals of sodic hyposulphite are easily procured ($\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}$). Many other hyposulphites may be obtained, but they are unimportant. The acid cannot be isolated, as it immediately begins to undergo decomposition into sulphur and sulphurous acid.

Exp. 165.—Add to a solution of sodic hyposulphite a little hydrochloric acid. In a few minutes a pungent smell of sulphurous acid will be perceived, while the liquid becomes milky from the deposition of sulphur—



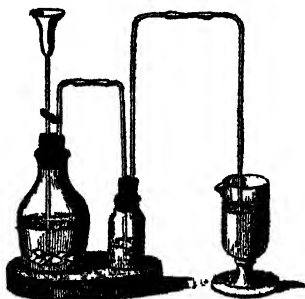
(34) SULPHURETTED HYDROGEN: *Symb.* H_2S ; *Atomic and Mol. Wt.* 34; *Mol. Vol.* ; *Sp. Gr.* 1.1912; *Relative Wt.* 17.

Exp. 166.—Place 10 or 15 grams of ferrous sulphide in small lumps in a gas bottle (*Fig. 62*), and pour upon it about 100 c. c. of diluted sulphuric acid (1 of acid to 6 of water): an effervescence, with escape of this offensive gas, immediately occurs—



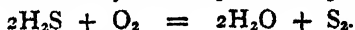
Other sulphides also furnish the gas—sulphide of antimony, for example, when heated with hydrochloric acid. This gas is often wanted in the laboratory for the analysis

Fig. 62.



of ores, and Fig. 62 shows a convenient mode of arranging the apparatus for liberating it. The small bottle contains a little water, through which the gas bubbles, in order to remove any particles of acid or of iron salt which may have been splashed over by the effervescence, before it is passed into the solution for analysis.

Sulphuretted hydrogen is colourless and transparent; it has a disgusting odour of rotten eggs, and is very poisonous if breathed. It is soluble in about one-third of its bulk of water, and the solution, which has the smell of the gas, is a useful test for certain metals. But if the solution be kept in bottles only partially filled, the oxygen of the air combines with the hydrogen of the compound, water is formed, and the liquid becomes milky from deposited sulphur—



Sulphuretted hydrogen burns in the air with a pale bluish flame, furnishing water and sulphurous anhydride. It contains its own bulk of hydrogen, and half its volume of the vapour of sulphur—

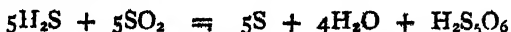


the three volumes of the constituents becoming condensed into two volumes, just as, in the analogous case of water, the two volumes of hydrogen and one volume of oxygen furnish two volumes of steam.

Sulphuretted hydrogen, though soluble, may be collected over warm water, if the gas be made in a retort or in a flask fitted with a gas tube. ✓

Exp. 167.—Fill two small bottles of 250 or 300 c. c. capacity with the gas; prepare a bottle of sulphurous anhydride of similar size; withdraw the stopper, and close the bottle with a glass plate. Do the same with one of the bottles of sulphuretted hydrogen, and invert the sulphurous anhydride over this bottle. The two gases will immediately, in the presence of the moisture, react on each other; the oxygen of the sulphurous anhydride uniting with the hydrogen of the sulphuretted hydrogen, while sulphur is deposited.

A little pentathionic acid ($\text{H}_2\text{S}_5\text{O}_6$) is always formed at the same time—

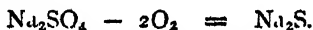


Chlorine, iodine and bromine also immediately decompose sulphuretted hydrogen, with separation of sulphur.

Exp. 168.—Repeat the experiment above described, substituting a bottle of chlorine for one of sulphurous anhydride: hydrochloric acid is formed, and sulphur is deposited—



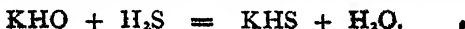
Sulphuretted hydrogen is often produced spontaneously under various circumstances. Whenever a soluble sulphate of the metal of one of the alkalis or alkaline earths is kept in contact with decaying organic matter, where air does not find free access, the sulphate becomes reduced to the form of sulphide, so that soluble sulphides become formed, the organic matter removing the oxygen and furnishing water and carbonic acid. The deoxidising action on sodic sulphate is as follows:



In this way soluble sulphides are formed in certain springs, such as those of Harrogate and Moffat, giving to them their nauseous odour; since the sulphuretted hydrogen is liberated by the action of even so feeble an acid as the carbonic—



Owing to the great tendency of sulphur to unite with metals the hydrogen in sulphuretted hydrogen may be readily replaced by metals forming *sulphydrates* or *sulphides*. Thus if the gas be passed into a solution of potash it is quickly absorbed and potassic sulphydrate is produced—



Since, however, potassic sulphydrate and potassic hydrate react to form potassic sulphide and water ($\text{KHS} + \text{KHO} = \text{K}_2\text{S} + \text{H}_2\text{O}$), the solution if only half saturated with sulphuretted hydrogen contains potassic sulphide.

156 *Sulphuretted Hydrogen and the Metals.*

A solution of ammonia, when saturated with sulphuretted hydrogen, is a useful test for metals, $2\text{H}_3\text{N} + \text{H}_2\text{S}$ yielding $(\text{H}_4\text{N})_2\text{S}$.

Metals the atom of which, like potassium, take the place of a single atom of hydrogen usually form two compounds with sulphuretted hydrogen, in one of which a single atom of the hydrogen is displaced by the metal, and in the other both atoms are displaced; for instance, we have—

Sulphuretted hydrogen	HHS
Hydric potassic sulphide	KHS
Dipotassic sulphide	KKS;

whilst metals of which the atom, like calcium, displaces two atoms of hydrogen form but a single compound when acted upon by the gas; as, for example—

Baric sulphide	BaS,
Calcic sulphide	CaS; and so on.

Certain metals may be precipitated from their acidulated solutions by sulphuretted hydrogen. Among these are silver, bismuth, mercury, lead, copper, gold, platinum, tin, antimony, and arsenicum; and the precipitate, which is usually in the form of a hydrate, often has a characteristic colour.

Exp. 169.—Prepare a solution of sulphuretted hydrogen in water, by passing a stream of bubbles of the gas through water for a few minutes. Add some of this solution to a dilute solution of tartarised antimony. a beautiful orange-coloured antimony sulphide is separated. With a dilute solution of stannic chloride, a yellow stannic sulphide will be formed; and with a solution of cupric sulphate, also largely diluted, a brownish-black cupric sulphide will be obtained.

Other metals are not precipitated from the acidulated solutions of their salts by sulphuretted hydrogen; among these are the salts of iron, cobalt, nickel, manganese, zinc, aluminium, and chromium. Hence it is customary, in the analysis of minerals, to employ sulphuretted hydrogen as a means of separating those metals above mentioned which are precipitated from their solutions by the action of the gas from those which are unacted upon by it.

In the case of those metals which are not precipitated from their acid solutions by sulphuretted hydrogen, the sulphide may generally easily be obtained by presenting an alkali metal to the acid radical at the same moment that the sulphur is presented to the metal which is required in the state of insoluble sulphide, and this is done by adding a soluble sulphide to the solution of the metallic salt. Ferrous sulphate, for instance, gives no precipitate with sulphuretted hydrogen, but it yields a black ferrous sulphide as soon as its solution is mixed with one of dipotassic sulphide—



Many of the sulphides of metals which are precipitated by the gas from the acid solutions of their salts are soluble in the solutions of the alkaline sulphides, owing to their power of forming double sulphides, which are soluble in water. Among these are the sulphides of gold, platinum, antimony, arsenicum, and tin, which may be dissolved out and separated from other sulphides such as those of copper, bismuth, lead, silver and mercury, by treating the mixed precipitates with a solution of dipotassic sulphide, in which the metals last enumerated are insoluble.

The smell of sulphuretted hydrogen is one of its several tests; very small traces of it may also be recognised by their power of blackening white paper moistened with a solution of acetate or other salt of lead.

Exp. 170.—Place a drop of a solution of lead acetate upon a piece of paper. Hold it for an instant near the open bottle of a solution of sulphuretted hydrogen. a black or brown stain of lead sulphide will immediately be produced.

(35) CARBON DISULPHIDE: *Symb.* CS_2 ; *Atomic Wt.* 76. —This is an extremely volatile liquid, usually of very offensive odour, due to some impurity. It exerts a poisonous action upon animals. It boils at 48° , giving off a remarkably inflammable vapour. It is considerably heavier than water, and is not soluble in it; but is very soluble in ether and

alcohol, as well as in the oils. It is one of the best solvents for the oils and fats, and is used largely for their extraction. It also freely dissolves sulphur, iodine, bromine, and phosphorus.

Exp. 171.—Place a few drops of the disulphide in three or four test-tubes. To one add a little powdered sulphur, to a second a minute scrap of iodine, to a third a fragment of phosphorus, and to a fourth a few drops of water. Notice the beautiful colour produced by the iodine, the solution of the sulphur and phosphorus, and the insolubility of the liquid in water.

Carbon disulphide is prepared on a large scale by driving the vapour of sulphur over glowing coke, and condensing that vapour in suitably cooled receivers. It is one of the few liquids which does not freeze at the lowest temperature hitherto obtained. This body combines with the sulphides of the alkali metals, and forms unstable compounds, which are in some respects analogous to the carbonates, but they contain sulphur instead of oxygen; K_2CO_3 being the carbonate, K_2CS_3 the corresponding sulphocarbonate.

Sulphur combines with chlorine in two proportions. One of these (S_2Cl_2) is a yellow liquid, the other (SCl_2) is of a deep red colour, and fumes strongly in the air. Both are decomposed by water.

2. SELENIUM. 3. TELLURIUM.

Sulphur belongs to a group of elements of which the other two, *selenium* and *tellurium*, are of rare occurrence, and are practically unimportant. All three elements are characterised by forming gaseous fetid compounds with hydrogen, containing two atoms of hydrogen to one atom of the characteristic element, and in each case the gas contains two volumes of hydrogen united with one volume of the vapour of the other element, the three volumes having become condensed into the space of two.

All the three elements have a strong attraction for oxygen, and they each furnish two oxidized compounds, which in combination with water have acid properties.

Sulphuretted hydro- gen (H_2S)	Sulphurous acid (H_2SO_3)	Sulphuric acid (H_2SO_4)
Seleniuretted hydro- gen (H_2Se)	Selenious acid (H_2SeO_3)	Selenic acid (H_2SeO_4)
Telluretted hydro- gen (H_2Te)	Tellurous acid (H_2TeO_3)	Telluric acid (H_2TeO_4)

The properties of selenium are intermediate between those of sulphur and tellurium; and this last has so much resemblance to the metals that it is usually described among them. Of the three, sulphur has the lowest and tellurium the highest atomic weight; and the specific gravity, the fusing point, and the boiling point increase in the same order as the atomic weights

CHAPTER VIII.

PHOSPHORUS GROUP

1. PHOSPHORUS 2 ARSENICUM 3. ANTIMONY 4. BISMUTH.

(36) 1. PHOSPHORUS *Symb* P, *Atom. Wt* 31, *Atom. Vol.* \square , *Sp. gr. of solid*, 1.83, *of vapour*, 4.42, *Rel Wt.* 62; *Mol. Wt* P_4 , 124, *Mol Boiling Pt.* 288°, *Fusing Pt* 44°

This remarkable element has considerable resemblance to the metals arsenicum and antimony. All three form fetid, inflammable, gaseous compounds with hydrogen, in which three atoms of hydrogen are united with one atom of the other element. Nitrogen has also a near relation to this group; but its hydrogen compound, ammonia, is strongly alkaline, while the hydrogen compounds of the other members of the group are very feebly so. Bismuth, though a member of this group, forms no compound with hydrogen. Each of the five elements is also distinguished by furnishing two compounds with oxygen, which, when combined with water, possess acid properties, except the lower compound

with antimony, which is feebly basic, and that of bismuth, which is more strongly basic.

Ammonia (NH_3)	Nitrous anhydride (N_2O_3)	Nitric anhydride (N_2O_5)
Phosphuretted hydrogen (PH_3)	Phosphorous anhydride (P_2O_3)	Phosphoric anhydride (P_2O_5)
Arseniuretted hydrogen (AsH_3)	Arsenious anhydride (As_2O_3)	Arsenic anhydride (As_2O_5)
Antimoniuretted hydrogen (SbH_3)	Antimonious anhydride (Sb_2O_3)	Antimonic anhydride (Sb_2O_5)
	Bismuth oxide (Bi_2O_3)	Bismuthic anhydride (Bi_2O_5)

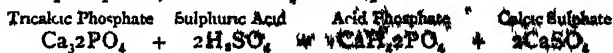
Arsenicum, antimony, and bismuth will be described with the metals.

Phosphorus is never found uncombined in nature. It occurs in small quantities in granite and the older rocks, in the form of tricalcic phosphate, or phosphate of lime. When these rocks crumble down and form soil, they supply phosphates to plants, which store them up in considerable quantity in their seeds. From the seeds the animals which feed upon them derive a sufficient quantity for their support. Phosphorus collects in the animal system in large quantities, and furnishes, as calcic phosphate, the principal earthy component of the bones. Phosphorus is also an essential ingredient in the brain and nervous tissue; and it passes out of the body constantly, in the form of soluble phosphates in the urine, and in the solid excreta as insoluble earthy phosphates. It is also abundant in guano, the excrement of seafowl.

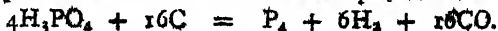
Phosphorus is now always extracted from calcic phosphate, which is generally obtained from bones.

Exp. 172.—Burn a few bones in the open fire. They will leave more than half their weight of a white ash. Grind this ash to a fine powder, and mix 30 grams of it with 20 grams of oil of vitriol and 180 or 200 grams of water. After standing for some hours, strain off the acid liquor from the calcic sulphate which is formed. Preserve this liquor for preparing some of the soluble phosphates.

The change in this experiment consists in the removal of two thirds of the calcium by the sulphuric acid, in the insoluble form of calcic sulphates, the bone earth, which is not soluble in water, becoming converted into a very soluble acid phosphate, as shown by the equation—



If phosphorus is to be made, a solution of the acid phosphate, or *superphosphate of lime*, prepared by a similar process, is evaporated down to a syrupy consistency, and mixed with about a third of its weight of powdered charcoal, after which it is heated nearly to redness. It is then placed in an earthen retort, and slowly raised to a full red heat. Phosphorus gradually comes over in vapour, and is condensed in water, while a large quantity of hydrogen and carbonic oxide gases pass off, leaving a considerable residue of bone earth in the retort. The superphosphate when heated with charcoal is decomposed. Its calcium retains sufficient phosphorus and oxygen to reconvert it into tricalcic phosphate, $3(\text{CaH}_2\text{2PO}_4)$ becoming $\text{Ca}_3\text{2PO}_4 + 4\text{H}_3\text{PO}_4$; while the phosphoric acid in the presence of the charcoal breaks up as follows—



The phosphorus is purified by melting it under warm water, heating it with chloride of lime, and forcing it, by pressure, through washleather; it is then moulded, while in the fluid state, by allowing it to flow into tubes, which are next chilled in cold water, and the phosphorus becomes solid.

Phosphorus is a soft, semi-transparent, waxy-looking substance, which fumes in the air, and forms white vapours, smelling something like garlic. The fumes are feebly luminous in a dark room, and become white, which means the 'light-bearer'. It has a sp gr of 1.83, and melts at 44° . It is extremely inflammable, and takes fire just above its melting point. On this account it must always be kept under water, and should not be handled with warm fingers.

Phosphorus is not soluble in water, but it is slightly so in ether; it is more soluble in benzol, oil of turpentine, and in the fixed oils.

Phosphorus is also known in two other allotropic forms, viz. white and red. White phosphorus is slowly produced upon the sticks of phosphorus when kept under water. The red form, or amorphous phosphorus, is prepared in large quantities by heating phosphorus for several hours to about 250° C. in closed vessels, filled with nitrogen or with carbonic anhydride. The melted phosphorus gradually becomes solid, opaque, and of a deep red colour, and its sp. gr. becomes increased to 2.14. In this form it is insoluble in carbon disulphide, which may be used to dissolve out the last traces of the common form. When quite free from ordinary phosphorus, red phosphorus may be exposed to the air without danger. It may be heated in the open air beyond 400° without taking fire; but if raised to about 280° it is changed into the common form, and bursts into a blaze. When heated in vessels full of nitrogen, it may be distilled like common phosphorus, the vapour condensing in clear, colourless drops.*

Exp. 173 — Dissolve 1 or 2 decigrams of phosphorus in 2 c. c. of carbon disulphide in a test-tube, pour a little of the solution upon a piece of filtering-paper, and allow it to dry. The phosphorus will be left in a finely divided form, and will so fire to the paper in a few minutes.

Red phosphorus is employed in preparing *safety matches*. The matches are covered with melted paraffine, and tipped with a paste consisting of potassic chlorate, antimonious sulphide, powdered glass, and gum water. When they are to be lighted, they are rubbed upon a surface covered with a mixture of red phosphorus with half its weight of powdered glass. Common lucifer-matches have the phosphorus mixed

* The vapour of phosphorus has twice as many atoms in its molecule as most elements, 4 atoms of phosphorus instead of 2 being contained in the molecule. Arsenicum resembles phosphorus in this respect.

up in the paste with which they are tipped, and these take fire when rubbed on any rough surface. The safety matches can only be kindled by friction on the phosphoric surface.

Exp. 174.—Place a bit of phosphorus in a solution of mercuric nitrate. In the course of a day or two it will be covered with brilliant crystals of reduced silver.

Solutions of salts of copper, platinum or gold will also yield up their metal if used instead of solution of a silver salt, owing to the strong attraction of phosphorus for oxygen.

Phosphorus combines with many of the metals when heated with them. Such compounds are called phosphides.

(37) Phosphorus forms two well-marked oxides—phosphoric anhydride (P_2O_5) and phosphorous anhydride (P_2O_3). They give powerful acids when combined with water, viz. phosphoric acid (H_3PO_4) and phosphorous acid (H_3PO_3), besides which, there is a third acid, the hypophosphorous ($H_2PH_2O_2$), with still less oxygen.

Phosphoric Anhydride (P_2O_5).

Exp. 175.—Dry two or three pieces of phosphorus the size of a pea upon blotting-paper, and place them upon a small capsule in the middle of a plate. Touch the phosphorus with a hot wire, and cover it at once with a dry gas jar. White flakes of the anhydride will be formed, and will settle down upon the plate.

This anhydride is a snow-white powder which attracts moisture quickly; it fizzes when a few drops of water are added to it; it dissolves quickly except in alcohol, and produces phosphoric acid, which is intensely sour, but not caustic—



It is easily made in large quantities by burning dry phosphorus in a dish hung in a large globe supplied with a current of dry air.

Phosphoric acid may be formed by dissolving phosphorus in about 13 times its weight of diluted nitric acid of sp. gr. 1.20. Concentrated acid must not be used, as it acts with

great violence. The phosphorus is then oxidized by the nitric acid, which is decomposed; and on boiling down the solution the excess of nitric acid is driven off, and pure phosphoric acid is obtained in solution. If the water be driven off as far as possible, the acid is left in a form which fuses at a low red heat, and becomes a clear, glassy-looking solid on cooling. This glass dissolves easily in water.

Besides ordinary phosphoric or orthophosphoric acid, as it is called, (H_3PO_4), two other distinct acids closely related to it are known, viz. metaphosphoric acid, (HPO_3); and pyrophosphoric acid, ($\text{H}_4\text{P}_2\text{O}_7$); each of these forms a special set of salts.

The ordinary phosphoric acid is prepared by dissolving phosphorus in nitric acid, as already described. If the glassy acid thus obtained be boiled with water, and made slightly alkaline with sodic carbonate, a salt is obtained, the *sodic hydric phosphate*, which on crystallisation gives efflorescent rhombohedra ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$).

Exp. 170. Take the solution of superphosphate of lime prepared as directed in Exp. 172, add sodic carbonate until the liquid is faintly alkaline; filter it from the precipitated calcic phosphate, and evaporate the solution till a drop of it crystallises when allowed to cool on a slip of glass. Then allow the whole solution to cool. Crystals of sodic hydric phosphate will be formed.

If the sodic hydric phosphate, or *rhombic phosphate*, as it is sometimes called, be mixed with an excess of caustic soda, a crystallisable salt, formerly called *metaphosphate* of soda, with the formula $\text{Na}_2\text{P}_2\text{O}_7 \cdot 12\text{H}_2\text{O}$, or *trisodic phosphate*, is obtained. If a quantity of phosphoric acid be divided into two equal parts, the first of which is just neutralized with sodic carbonate, and then the other half of the acid is added, a third salt is obtained, which crystallises with difficulty. It was formerly known as *metaphosphate of soda*. It is the *disodic metaphosphate*, ($\text{Na}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$).

Thus it is possible to form three different sodium salts

Sodic Phosphates.

from the common phosphoric acid, in which the hydrogen of the acid is displaced by the sodium.

Tribasic phosphoric acid
Dihydric sodic phosphate
Hydric disodic phosphate
Trisodic phosphate

H_3PO_4
 NaH_2PO_4
 Na_2HPO_4
 Na_3PO_4

These salts all give a yellow precipitate with argentic nitrate, or triargentic phosphate (Ag_3PO_4). They also give when mixed with ammonia and magnesium sulphate, a white line precipitate of ammonio magnesium phosphate ($Mg_2PO_4 \cdot 6H_2O$).

Exp. 177.—Dry a portion of the dihydric hydric phosphate crystals at $150^\circ C$. They will lose their water of crystallization and leave a white mass.

This consists of Na_2HPO_4 . If it is redissolved in water, it will furnish the original salt, known by its property of precipitating silver nitrate yellow—



As a triargentic phosphate, the solution will combine with nitric acid, and will reddens litmus.

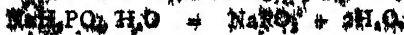
Exp. 178.—Take a portion of the same solution, and add it to redness in a porcelain dish, before redissolving in water.

The result will now be different: the white mass of the salt coalesces, and loses a molecule of water, becoming $Na_2P_2O_7 + H_2O$. If the solution is redissolved in water, the salt may be crystallized with $10H_2O$.

Exp. 179.—Add a portion of the solution to one of argentic nitrate, and a white precipitate will be formed, $Na_2P_2O_7 + 4AgNO_3$ becoming $Ag_4P_2O_7 + 2NaNO_3$.

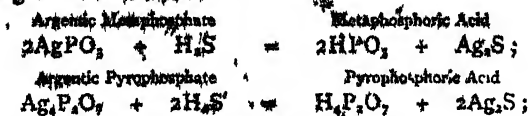
This white salt is the pyrophosphate, so called, because obtained by the fusion of the common phosphate.

Exp. 180.—Heat a little of the pyrophosphate to redness, if sufficient to convert it into a glassy mass of anhydrous phosphate, the elements of water being expelled—



This salt belongs to a class known as the metaphosphates, which are recognised by precipitating argentic nitrate white and gelatinous, and redissolving the precipitate if an excess of the phosphate be used.

The pyrophosphoric and the metaphosphoric acids may even be obtained in solution in water by decomposing the silver or lead salts of their acids by means of sulphuretted hydrogen. For instance—



the silver and the hydrogen changing places.

The ordinary triargentic phosphate would yield the common form of the acid—



Acids which, like the metaphosphoric, contain one atom of hydrogen, capable of displacement by a metal, are called *monobasic acids*. Those in which there are three atoms of hydrogen which admit of displacement by hydrogen, like the ordinary form of phosphoric acid, are called *tribasic acids*; while in such cases as the pyrophosphoric, which contain four atoms of displaceable hydrogen, the acid is said to be *tetrabasic*.

The phosphorous and hypophosphorous acids are of little importance.

(37*) With hydrogen phosphorus forms three compounds: one solid (HP_3); one liquid (H_{10}P_3), the vapour of which inflames immediately on reaching the air; and a gas (H_3P). This is the only hydride of phosphorus that we shall describe.

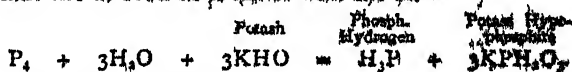
PHOSPHURETTED HYDROGEN: *Synth.* H_3P ; *Atom. and Mol. Wt.* 34; *Sp. Gr.* 1.185; *Rd. Wt.* 17.

This is a poisonous gas, with a disgusting odour of garlic, highly inflammable, and liquefiable under pressure. It is decomposed by chlorine, and, though not soluble in water,

is wholly absorbed by a solution of bleaching powder. It precipitates the salts of lead and copper black (forming phosphides), and corrosive sublimate yellow.

Lap 181.—Dissolve 4 grams of caustic potash in 20 grams of water, place it in a small retort of about 50 c.c. capacity, and add 2 or 3 decigrams of phosphorus; immerse the neck of the retort just below the surface of water in a small capsule, and heat the mixture gently. Bubbles of gas will form in the retort, and will break with a flash and a slight explosion upon the surface of the potash solution. By degrees the air of the retort will be deprived of all its oxygen, and then the bubbles of gas, as they escape into the air, will take fire, producing a white wreath of phosphoric anhydride, which forms a number of ringlets, revolving in vertical planes around the axis of the wreath itself as it ascends.

In this beautiful experiment, which requires care, lest the retort be broken by the bursting of the bubbles within it, phosphuretted hydrogen gas is formed, accompanied by traces of the vapour of the liquid phosphide, which causes it to take fire as soon as it mixes with the air.



Pure phosphuretted hydrogen, which does not take fire spontaneously, is obtained by heating phosphorous acid, which breaks up into phosphoric acid and phosphuretted hydrogen—

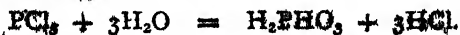


Phosphuretted hydrogen is feebly alkaline in its nature, which is in some measure analogous to that of ammonia, to which it corresponds in composition, but it contains only half a volume of phosphorous vapour and three volumes of hydrogen in two volumes of the gas.

Phosphorus burns when placed in chlorine gas. When the chlorine is in excess, it forms a solid volatile chloride (PCl_5), which, when put into water, produces phosphoric and hydrochloric acids—



If the phosphorus is in excess, a liquid chloride (PCl_3) is formed; and this furnishes with water phosphorous and hydrochloric acids—



There are corresponding bromides of phosphorus.

CHAPTER IX.

SILICON AND BORON.

(38) Silicon, in combination with oxygen as silica or silex, is the most abundant solid material found upon the earth. It forms the essential substance of flint, sea sand, sandstone, quartz, agate, and calcedony, besides entering largely into the composition of clay, and a great number of crystallised minerals, and nearly all the common rocks, except limestone.

SILICON—*Symb.* Si; *Atom. Wt.* 28; *Sp. Gr.* 2.49—is never found uncombined, but is always obtained by chemical means, one method being the heating of sodium in the vapour of silicic chloride (SiCl_4), when common salt is formed and silicon is set free. It is a brown powder, which burns when heated strongly in air or oxygen, but which at a very high heat, though below that required for fusing steel, may be melted if excluded from air. It may be obtained crystallised in plates and octahedra, which are hard enough to scratch glass.

Silicon forms only one oxide, viz. *silica* (SiO_2), and this is found both crystallised and amorphous. Pure crystalline silica has a sp. gr. of 2.642. It occurs in *quartz* in six-sided prisms, ending in six-sided pyramids. *Amethyst* is a purple variety of quartz. The amorphous form of silica has a sp. gr. of only 2.2; it may be obtained by melting quartz before the oxyhydrogen blowpipe. *Calcedony* is a mechanical

mixture of crystalline and amorphous quartz. *Agate* consists of a succession of layers of crystalline and amorphous silica. *Flint* is a form of chalcedony chiefly found in the upper chalk; and *opal* is a hydrated variety of amorphous silica.

Silica, when once crystallised, is insoluble in water, and in all acids except the hydrofluoric.

Silica, in fine powder, looks like a white earth, but it has a strong tendency to unite with bases, a property which may be employed to obtain it in a pure form.

Exp. 182.—Place about 60 grains of a mixture of potassic and sodic carbonate in a clay crucible, and raise it to a red heat; when fused add 15 grains of ground flint or of fine sand to the melted mass: effervescence is produced slowly, due to the escape of carbonic anhydride, and the silica is gradually dissolved. When the decomposition is over, pour out the mass on a cone slab, and after it has cooled let it digest in water: most of it will dissolve, with the exception of some impurities, such as oxide of iron.

The solution thus obtained consists of a mixture of silicates of potash and soda, with a large excess of the alkalis.

A smaller proportion of alkali might have been used, but it would have required a stronger heat to melt the silicate, and the product would have been less easily soluble.

Exp. 183.—Add gradually to a portion of this solution dilute hydrochloric acid in excess: the mass becomes partly or wholly redissolved, but on evaporating the silica separates at first as a jelly-like hydrate, and this, by further drying, becomes converted into a white earthy-looking powder, no longer soluble in acids. Wash the dry mass with water as long as anything is dissolved, the soluble chlorides may thus readily be removed, leaving silica in a nearly pure state, in the amorphous form.

Exp. 184.—Heat some common flints to redness in the fire, and suddenly quench them in water. They become very friable, and are easily reduced to a fine powder. Heat this, add hydrochloric acid, and wash thoroughly, and the result is nearly pure silica.

Exp. 185.—To another portion of the solution of silica in the alkalis add hydrofluoric acid in excess, so as to redissolve the

whole. Place the clear solution in a shallow tray formed by tying a piece of parchment paper over a hoop of wood or of gutta percha, 10 or 12 cm. in diameter, and float this little vessel in a dish of water. The acid and saline substances are separated by *dialysis* from the silica, and pass out into the water. If the water in the dish be changed twice a day, the liquid left in the hoop will, in three or four days' time, be found to consist of a solution of pure silica in water, and may be further concentrated by cautious evaporation.

In this experiment the parchment paper, or dialyser, retains the *colloid*, or gelatinous form of silica, while it allows the *crystalline* and acid particles to pass through its pores into the water on the other side.

The solution of silica is tasteless, limpid, and colourless; but if the evaporation be carried too far, the silica separates in the form of a jelly.

Finely divided silica may be gradually dissolved by boiling it with the alkalis or their carbonates, and even flints in their unground condition may be dissolved in strong solutions of caustic alkali if the solution be digested upon them under pressure. The Geysers, or hot springs of Iceland, contain large quantities of silica dissolved, and as the liquid cools deposit a considerable portion upon objects exposed in the stream. They are then often said to be 'petrified,' or converted into stone, the silica being deposited in the interstices, and preserving the appearance of the original structure.

(39) *Silicates: Glass*.—The silicates are very abundant natural productions. Silica combines with bases in several different proportions, and forms a great variety of crystallised minerals, many of which are double silicates of complex nature.

Glass consists of a mixture of several silicates, which, when heated to a particular temperature, are plastic and viscous, and retain their transparency on cooling. The nature and proportions of the silicates present are made to vary according to the use to which the glass is to be applied. The degree

of fusibility of the silicates varies widely. Fire-clay, or aluminic silicate ($\text{Al}_2\text{O}_3, 2\text{SiO}_2$), is nearly infusible in the furnace, and it is the material of which fire-bricks and crucibles are made. Calcic silicate is also very infusible, whereas the ferrous silicate ($\text{FeO}, 2\text{SiO}_2$) constitutes the 'bull-dog' or fusible slag, of iron refiners. Lead silicate ($2\text{PbO}, 3\text{SiO}_2$) is still more fusible, and furnishes a clear yellowish glass. The silicates of potash and soda are also very fusible. All these silicates, when mixed with each other, melt at much lower temperatures than they do when separate. Many of them, when thus melted, possess the exceptional property of viscosity, between the point of perfect liquidity and solidification. It is this viscous condition which enables glass to be moulded into the countless forms required for art or luxury. Good glass also has the valuable property of not crystallising as it cools, in certain cases some of the silicates, however, do crystallise out, and then the glass becomes opaque, and though the separate silicates of which it consists are more or less readily attacked by water and acids, if the proportions of the mixture are properly selected, glass formed from these silicates is no longer soluble. The different varieties of glass are not to be regarded as definite compounds, but as mixtures in varying proportions of their component silicates, which, however, in the best kinds generally approach some simple atomic proportions.

Much care is requisite in selecting the materials for the finer kinds of glass. Potash is preferred to soda, because the glass made from soda has a bluish green tinge. Soda gives a more fusible glass. The addition of lime increases its hardness and lustre, but diminishes its fusibility. An excess of lime is apt to make it milky-looking.

1. Window glass, or crown glass, is made of a mixture of silicates of soda and lime. 100 parts of pure white sand, 35 or 40 of chalk, 30 of soda ash, and from 50 to 150 of broken glass, or *cullet*, are the proportions often used. The mixture is heated gradually, to prevent it from frothing up, and is after-

wards raised to a very intense heat. Plate glass contains the same materials in different proportions. 2. Bottle glass contains a smaller proportion of silica than either window or plate glass, and is made of much coarser materials. It consists of a mixture of silicates of soda, lime, alumina, and iron. 3. Bohemian glass, which is very hard and infusible, is a mixture of silicates of potash and lime. It is used for making the combustion tubes employed in the analysis of organic substances, and hence is much prized in the laboratory. 4. The ordinary white, or *flint glass*, consists almost entirely of silicates of potassium and lead. The proportions of materials used are—300 of fine sand, 200 of red lead, 100 of refined pearl ash, and about 50 parts of nitre. The oxide of lead renders the glass much heavier and more fusible, giving it a higher refractive and dispersive power upon light, and greater brilliancy, but it makes it softer and more easily tarnished, and it is also liable to be corroded by alkaline solutions.

Glass, when melted, dissolves many of the metallic oxides without losing its transparency, but becomes coloured with tints varying according to the metallic oxide employed. Cobalt gives a splendid sapphire blue, manganese a violet, uranium a yellow, ferrous oxide a green, ferric oxide a yellow or reddish-brown, cupric oxide a green, and cupreous oxide a ruby-red.

Well made glass is not acted on by any acid or mixture of acids, except the hydrofluoric, which last removes its silica, but it is not quite insoluble. If left long in water, or buried in moist earth, it becomes slowly decomposed. This is often seen in wine bottles, which exhibit the brilliant colours of thin plates, due to the scaling off from the surface of flakes detached by slow chemical action of moisture.

Exp 186—Grind a little glass to a fine powder in a mortar, place it on a piece of moistened turmeric paper: sufficient alkali will be dissolved by the water to tinge the turmeric brown.

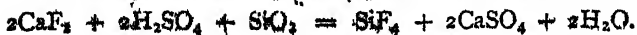
If glass articles are allowed to cool rapidly by exposing them while red hot to the air, they become inconveniently brittle. The outer surface becomes solid, whilst the inner portion remains dilated by the heat: as the mass cools, the particles within, by their adhesion to the external solid portion, are still held in their dilated state. A very slight force, such as a scratch on the surface, or the change of temperature from a cold room to a warm one, will often cause them to crack. In order to avoid this inconvenience, the glass is annealed, or placed in a chamber heated nearly to redness, where the material is allowed to cool very slowly, by which means the particles are enabled to assume their natural position with regard to each other.

Glass, however, is a bad conductor of heat, but dilates considerably when heated, so that even after annealing it is liable to crack when exposed to sudden changes of temperature, such as that produced by pouring boiling water into a cold glass, especially if it be thick.

Exp. 187.—Take one of the drops of glass formed by allowing melted glass to fall into water, and suddenly nip off the tail: the glass flies to pieces with a kind of explosion, and is reduced almost to powder.

Exp. 188.—Grind 3 or 4 grains of fluor spar to fine powder, and mix it with an equal weight of powdered glass or fine sand. Introduce it into a Florence flask previously fitted with a sound cork and a tube bent downwards for delivering gas. Pour upon the mixture about 30 grams of oil of vitriol, insert the cork and tube, and apply a gentle heat: a densely fuming gas is disengaged, consisting of silicic fluoride.

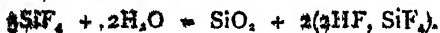
The change that takes place may be thus represented—



The gas (SiF_4) must not be inhaled, as it is very irritating, and produces coughing. When dry, it is colourless and transparent. Water produces a remarkable change in it.

Exp. 189.—Pass the gas into a glass of water. Each bubble as it rises becomes coated with a white opaque film, composed of

hydrated silica, while the liquid becomes intensely acid, from the formation of a new acid (the hydrofluosilicic), water being decomposed at the same time—



It is owing to the strong tendency to the formation of silicic fluoride that hydrofluoric acid corrodes glass so rapidly.

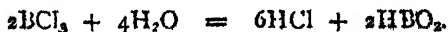
Silicon also forms a compound with chlorine (SiCl_4), and with bromine (SiBr_4), both of which are volatile liquids which are decomposed by water. A remarkable gaseous compound with hydrogen (SiH_4) is also known. It takes fire as soon as it escapes into the air, and may be procured, mixed with hydrogen, by decomposing a compound of silicon and magnesium by means of hydrochloric acid.

Silicon belongs to the group of tetrad elements: it has certain points of resemblance with the rare substances titanium and zirconium on the one hand, and with carbon on the other. All these elements form volatile compounds with four atoms of chlorine (CCl_4 , SiCl_4 , TiCl_4 , ZrCl_4). These chlorides are colourless liquids, except zirconic chloride, which is solid.

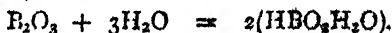
(39 *a*) BORON: *Symb.* B; *Atom.* IV. 11.

This is the characteristic element in boracic acid, which enters into the formation of borax, the sodium salt of this acid. It is an olive brown powder, which may be obtained by fusing 5 parts of boracic acid with 3 of sodium in a covered iron crucible, previously made red hot, covering the mixture with three parts of common salt, previously fused, and broken into coarse powder. An intense action occurs, and the mass becomes melted. It is to be poured in this red-hot condition into a large and deep vessel containing water acidulated with hydrochloric acid. The boron remains undissolved. By fusing it with aluminum, in which metal it is dissolved, boron has also been obtained in crystals, which are transparent, and nearly as hard as

diamond. This element is remarkable for its power of combining directly with nitrogen when heated in the gas, forming a grey powder. When heated with chlorine it burns freely, and combines with it, furnishing a gas (BCl_3), which is immediately decomposed by water into boracic and hydrochloric acids—



Boracic Anhydride (Symb. B_2O_3) is the only known oxide of boron. It combines with water, and then forms boracic acid, which crystallises in white, pearly-looking scales ($\text{HBO}_2, \text{H}_2\text{O}$) ; for—



The most abundant source of boracic acid is the district called the Maremma, in Tuscany, where it occurs in the uncombined state. It issues in small quantities in the jets of steam called *soffioni*, which are produced by volcanic heat. These jets are ducted into basins formed of brickwork and filled with water, when the steam is condensed, and a weak solution of boracic acid obtained. This solution is concentrated in shallow pans by the heat of the jets of steam themselves, ducted beneath them, and the acid is finally crystallised out on cooling.

Borax ($\text{Na}_2\text{O}, 2\text{B}_2\text{O}_3, 10\text{H}_2\text{O}$) is the most important salt of the acid. It is a natural production obtained by the drying up of certain lakes of Thibet, and it has lately been found in California and in some other localities. The crude Indian borax is called *tincal*. Borax is used as a flux in soldering, as it dissolves most metallic oxides and leaves a clean surface of the metal : it is often added to enamels, for the purpose of rendering them more fusible, and is used by the refiner in melting gold and silver, for making his crucibles less porous, and for rendering the collection of the metal more easy.

Exp. 190.—Bend the end of a piece of thin platinum wire, 8 or 10 cm. long, into a small hook; heat the wire to redness, and

instantly touch a crystal of borax as large as a split pea with the wire: it will adhere to the wire. Then introduce the wire and crystal into the flame of a spirit lamp. The borax will swell up, become opaque and white, and will then melt into a clear glassy bead.

Borax dissolves many metallic oxides when melted with them, and hence is often used as a test before the blow-pipe (Fig. 66).

Exp. 191.—Touch the bead just made with a wire moistened with a solution of cobalt nitrate. Then melt the borax again in the flame. A beautiful blue bead is obtained, which is almost opaque if the quantity of cobalt be considerable. If a scarcely visible fragment of manganese oxide be used, a purplish bead is obtained.

Boracic acid is easily obtained from borax.

Exp. 192.—Dissolve 40 grams of borax in about 4 times its weight of boiling water; add to the hot solution 10 grams of oil of vitriol, previously mixed with its own bulk of water. Sodic sulphate is formed, and remains in solution, while pearly crystals of boracic acid are deposited as the liquid cools. Pour off the solution, dry the crystals by pressure between pieces of blotting-paper. Place a few of them on a slip of platinum foil, and heat them in the flame of a spirit lamp. Water is driven off, and the anhydride which is left melts into a clear glass.

Exp. 193.—Dissolve a few crystals of the boracic acid in a small dish with a teaspoonful of alcohol. Set fire to the spirit: it burns with a green flame, which is a good test for boracic acid. A similar green flame is obtained if a crystal of borax be moistened with sulphuric acid and alcohol added, and kindled as before.

This green flame, when seen in the spectroscope, contains a series of peculiar green bands.

Boron forms with fluorine a gaseous *trifluoride* (BF_3), which is easily obtained by heating boracic anhydride with twice its weight of powdered fluor spar to redness in an iron tube.

Boron belongs to the class of triad elements, but in many properties it resembles silicon more than any other element.

CHAPTER X.

COAL GAS, AND OTHER COMPOUNDS OF CARBON.

(40) The two elements carbon and hydrogen furnish by their union a very numerous series of compounds, of which some are gaseous, some liquid, and some solid. They have received the general name of *hydrocarbons*; but the full study of these remarkable substances belongs to the division of chemical science known as organic chemistry, since they are, practically, always derived from the decomposition of bodies of organic origin.

Many of these bodies consist of absolutely identical proportions of the two elements, though they differ widely in properties. When compared together in their gaseous state they differ in density, so that the number of atoms of the elements in the molecule of these compounds must be different, although on analysis they yield the same proportions of each element. Let us take, for instance, a few of the many compounds of which 100 parts consist, of 85.71 of carbon and 14.29 of hydrogen :

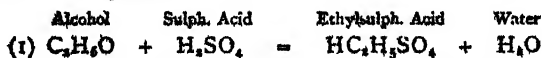
11.19 litres of olefiant gas	(C_2H_4)	weigh 14 grams
" oil gas	(C_4H_8)	" 28 "
" octylene gas	(C_8H_{16})	" 56 "
" cetylene gas	($C_{16}H_{32}$)	" 112 "

The density of oil gas is double that of olefiant gas; whilst that of octylene is double that of oil gas, and cetylene is double that of octylene. Such bodies are said to be *polymeric*.

OLEFIANT GAS (or *Ethylene*): *Symb.* C_2H_4 ; *Atom. and Mol. Wt.* 28; *Sp. Gr.* 0.978; *Rel. Wt.* 14.

Exp. 194.—Introduce into a retort which will hold a litre 30 c. c. of alcohol and 60 c. c. of oil of vitriol. Heat the mixture, and collect the gas over water; continuing the experiment until the mass blackens and swells up considerably. The gas consists at first chiefly of olefiant gas, mixed with ether vapour; but towards the end it becomes mingled with sulphurous anhydride.

The production of olefiant gas is due to the removal of the elements of water from the alcohol by the action of the acid. This occurs in two stages; in the first of which ethylsulphuric acid is formed, and in the second stage this body is decomposed—



And ethylsulphuric acid, when heated, is decomposed—

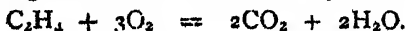


becoming olefiant gas (C_2H_4) and sulphuric acid (H_2SO_4).

Olefiant gas has no colour, but a faint sweetish smell, as of garlic. It is but little soluble in water. Under great pressures it may be liquefied, but has not been frozen. It is combustible, but will not support life.

Exp. 195.—Plunge a lighted taper into a small jar of the gas. The taper will be extinguished, but the gas will burn at the mouth of the jar with a bright smoky flame.

If mixed with three times its bulk of oxygen, it explodes violently by the action of flame or of the electric spark. If care be taken, the gas may be analysed by this means: steam is formed and immediately condensed, the 4 volumes of the mixture giving 2 volumes of carbonic anhydride—



Exp. 196.—Mix half a litre of the gas with the same quantity of chlorine, and let the mixture stand over water: the two gases combine slowly and form drops of a yellowish liquid, which collect on the surface of the water, and sink to the bottom as they increase in size.

The name *olefiant*, or 'oil-maker,' gas was derived from this circumstance, and the liquid itself, which was discovered by some Dutch chemists, is called *Dutch liquid* ($C_2H_4Cl_2$).

Exp. 197.—Mix half a litre of olefiant gas in a tall jar with a litre of chlorine, and, having closed the jar with a glass plate, mix the gases by agitation; then apply a light. The mixture will burn quietly, with the formation of a dense black smoke.

The chlorine in this case combines with the hydrogen, forming hydrochloric acid, while the whole of the carbon is separated—

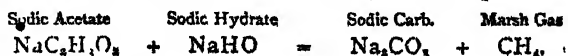


Olefiant gas is one of the substances found in coal gas, and is among the gases given off when fats and rosin are decomposed by heat.

MARSH GAS: *Symb.* CH_4 —or *Methyl Hydride* (CH_3, H)—*Atom. and Mol. Wt.* 16; *Sp. Gr.* 0.55; *Rel. Wt.* 8.

This is the simplest of the compounds of carbon with hydrogen. It is easily obtained, in an impure state, mixed with nitrogen and carbonic anhydride, by stirring the mud of stagnant pools, when it rises in bubbles to the surface, as a result of the decomposition of vegetable matter. It is also abundant in coal gas, as it is one of the substances most frequently produced by the distillation of organic matters at a high temperature. It is this gas which escapes from the seams of coal, and which, when mixed with air, fills the workings of the mines with the inflammable material known as *fire-damp*, and this gives rise to the disastrous explosions which occur from time to time in our collieries.

Marsh gas may be obtained pure by distilling one of the acetates with a hydrated alkaline base; for example:



Half the carbon remains behind as carbonate, with the whole of the oxygen in combination with the base; while the other half of the carbon unites with the whole of the hydrogen to form marsh gas.

Marsh gas has neither colour, odour, nor taste. It does not support life, but is ~~not~~ poisonous if breathed when mixed with air. It is but very slightly soluble in water, and has not been liquefied either by cold or pressure. It burns with a yellowish flame. It requires twice its bulk of oxygen for complete combustion, and then explodes with the forma-

tion of its own bulk of carbonic anhydride, the steam which is formed becoming immediately condensed, the three volumes of gas before combustion becoming one afterwards—



If a mixture of about 10 volumes of air with 1 of marsh gas be made, it will contain the quantity of oxygen necessary for complete combustion, and will explode powerfully on the approach of a light; 8 volumes of nitrogen and 1 of carbonic anhydride will be produced, while the steam will be immediately condensed. Hence the *after-damp*, or air left in a mine after an explosion has occurred, is entirely unfit for the support of human life; so that persons exposed to its influence perish as surely as they do from the direct effects of the flame.

Marsh gas, mixed with less than between two and three times its bulk of air, does not explode on the application of flame; and, if diluted with more than 18 or 20 parts of air, it only burns rapidly, but does not explode with sudden violence.

Sir H. Davy's safety lamp was contrived for the purpose of preventing these calamitous explosions in mines. Marsh gas requires a high temperature to set it on fire; so that, to kindle it, a substance must be not merely red hot, but nearly white hot.

Exp. 198.—Twist a piece of rather thick platinum wire 5 or 6 times round a thin glass rod, so as to form a coil at one end of the wire; hold this coil in the flame of a spirit lamp until it is red hot, then instantly place it in a jet of coal gas which is not burning, but is allowed to escape into the air. The wire will continue to glow without kindling the gas.

Exp. 199.—Place a sheet of iron or copper wire gauze, containing about 100 meshes in a square centimetre, over the flame of a spirit lamp; the flame will not pass through the gauze, owing to its being cooled down below its inflaming point. A piece of coarse gauze containing from 4 to 9 meshes in the sq. centim. will not prevent the flame from passing through.

Sir H. Davy's safety lamp is merely an oil lamp, enclosed

within a cylinder of fine wire gauze provided with a double top, and with a crooked wire passing up through the body of the lamp to trim the wick. When such a lamp is introduced into an atmosphere containing fire-damp, the flame is seen to enlarge until, when the proportion of marsh gas becomes large, it burns on the inner surface of the cylinder. Whenever this pale enlarged flame is seen, the miner must withdraw; for though no explosion can occur while the gauze is sound, yet the metal at that high temperature becomes corroded, and might easily break into holes, and a single large hole would be sufficient to cause an explosion.

Flame is never produced by a burning body, unless that body is converted into vapour before it burns; charcoal and iron, for instance, are not volatile, and they do not burn with flame; but phosphorus, sulphur, and zinc, all of which are volatilised before they take fire, burn with flame. Flame is hollow, and contains unburned combustible matter within, forming in fact a sort of luminous bubble.

Exp. 200.—Support one end of a glass tube, 12 or 14 cm. long and 6 or 8 mm. in diameter, just above the wick in the flame of a lighted candle. Vapours will pass up the tube, and may be burned at the other end.

The light and heat of flames are not proportioned to each other. The oxyhydrogen jet is the hottest flame known, but it gives out scarcely any light. If, however, a little solid matter, such as a piece of lime or the stem of a tobacco-pipe, be introduced, the light becomes very intense, although the effect of these solids is to lower the temperature of the flame. At high temperatures a solid body, when heated, even though it does not burn, gives out light. At first the light is dull red; as the heat increases it becomes yellow, then full white, and, when extremely intense, it has a tinge of violet. All our common luminous flames contain carbon in the solid state, which, when heated strongly, gives out light.

Exp. 201.—Place a cold saucer in a jet of burning coal gas: it is quickly covered with soot. Do the same in a candle flame:

the saucer is blackened. Try the experiment with the scarcely luminous flame of a spirit lamp; no soot is formed.

The deposit of soot is occasioned by the decomposition of olefant gas and marsh gas under the influence of a high temperature, hydrogen is partially separated from the carbon, and, being more inflammable, burns first, heating the carbon intensely. If the carbon reach the oxygen of the air at this high temperature, it burns away also; but the cold surface cools it before it enters into combination, and so it is deposited.

Exp. 202.—Kindle a common Argand gas-burner and place a glass chimney over it. Observe the strong light it gives out. Remove the chimney, blow out the flame, replace the chimney, covering the upper end with a cap of fine wire gauze, then kindle the gas above the gauze. The gas will have become mixed with air, it will burn quietly above the gauze, but will not give out light, nor will it smoke a cold saucer.

The air burns the carbon and hydrogen together before they can separate. What is called Bunsen's burner acts upon

a similar principle, it consists of a jet of gas (*a*, Fig. 63), which is surrounded by a tube of metal (*c*) at the bottom of which are openings for the admission of air (*b*), the gas passes up the tube, and becomes mixed with the air which enters at the openings near the bottom, and it burns without smoke when kindled at the top.

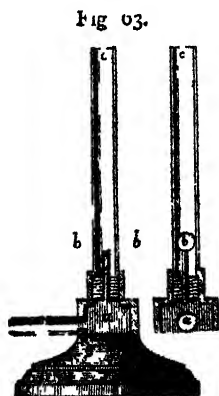


Fig 64.

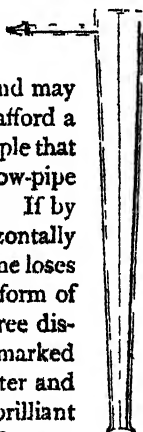


A sufficient supply of gas must be kept up, or else the flame will recede into the tube, and the gas will burn at the bottom.

The structure of flame may be examined easily in the flame of a candle. It will be seen to consist of several distinct portions, as shown in Fig 64.

The flame is maintained by the decomposition of the melted wax or tallow which rises in the wick, where it is converted into gases by the heat. At the lower part of the flame these gases become at once mixed with atmospheric air, no separation of carbon occurs, and they burn with a pale blue light at *a*. The greater part of the combustible vapours are still unburned; they rise above the wick, and form the central dark part of the flame *b*. Here they are decomposed by the heat produced by the combustion of the parts below. This heat causes the separation of solid particles of carbon, which become intensely hot, and give out light chiefly in the part marked *c*. This carbon itself burns away gradually as it rises to the surface of the flame, where it meets with fresh oxygen, and disappears in the form of transparent carbonic anhydride *d*.

Fig. 65.



By directing a jet of air into a flame the combustion may be rendered more active, and may be concentrated into a small space, so as to afford a very high temperature. It is upon this principle that that very useful instrument the mouth blow-pipe acts. Fig. 65 shows a convenient form of it. If by its means a current of air be directed horizontally across the flame a little above the wick, the flame loses its brilliancy, and is thrown to one side in the form of a beautiful pointed cone (Fig. 66), in which three distinct parts are visible. In the centre is a well-marked blue cone ending at *a*; outside this is a whiter and more luminous cone, and again outside this brilliant cone, which ends at *b*, is a third pale yellow flame *c*. The different parts of the flame vary in the effects which they produce; the blue cone is produced by the complete combustion of part of the vapour in the excess of oxygen supplied by the jet of air to that part of the flame. Beyond this the combustible vapour continually rising from the wick forms the luminous portion, which is very hot, and from

its containing an excess of combustible matter, is ready to take oxygen from any substance which is exposed to it. It is called the *reducing flame*. At the outer point of the flame the effects are reversed; atmospheric oxygen is carried for-

Fig. 66.



ward by the jet of flame, and becomes heated by it, so that an *oxidising* action occurs: if a fragment of a metal be exposed to the action of this part of the flame, it will be converted into oxide.

Exp. 203.—Introduce a small piece of common flint glass tube into the *reducing flame*, between *a* and *b* (Fig. 66), obtained by blowing gently through a candle flame. The glass will become opaque and black, because the lead will be reduced from the transparent form of oxide to the opaque condition of metal. When this has happened, place the black portion just in front of the oxidating flame at *c*. The discolouration will slowly disappear, and the lead will recombine with oxygen from the air, and again become transparent.

In skilful hands the blowpipe enables the observer to obtain quickly results of great value. Many compounds, when heated on a piece of charcoal in the reducing flame, immediately yield up their metallic basis; and by the colour of the little bead, and its malleability or brittleness, it may easily be known what metal is present.

Sometimes when the body does not yield a metal readily, a platinum wire, *d* (Fig. 66), bent into a hook at one end, forms a convenient support for the substance, which should not exceed a mustard seed in bulk. It will easily be ascertained whether the substance melts; whether it yields a transparent an opaque, or a coloured bead; whether it changes the

colour of the flame, and whether the effect of the reducing flame differs from that of the oxidating flame upon the body under examination.

A little borax or phosphate of sodium and ammonium, commonly called microcosmic salt, sometimes assists the examination.

When the substance is placed on charcoal sodic carbonate furnishes a flux which is often very useful.

Exp. 204.—Select a small stick of charcoal, and with the point of a knife make a small cavity of the size of a split pea upon the side near one end. Put a little white lead in the cavity, and heat it before the blowpipe in the reducing flame. A little bead of lead will easily be obtained, surrounded by a border of yellow lead oxide. The lead will flatten under the hammer.

Exp. 205.—Place in a cavity in another piece of charcoal a small fragment of copper oxide, with about its own bulk of sodic carbonate. The metal will require a stronger heat, but may be reduced in like manner. If the little bead be placed between two folds of paper it may be flattened with the hammer, and will show the red colour of copper.

Coal gas.—Certain kinds of coal, such as cannel coal and the bituminiferous house coal used in London, when heated, undergo decomposition, their constituents rearrange themselves in new forms, and give out a large quantity of gas, which burns with brilliant jets of flame. If such coal, instead of being allowed to burn in the open fire, is heated out of the air in iron or clay retorts provided with an escape-tube, a large quantity of gas may be collected, and may be used for illuminating or heating purposes. This is the common process of making coal gas. The products obtained by heating coal in this manner are very numerous. The solid residue in the retort, after the volatile matters have been driven off, constitutes 'gas coke.' Among the volatile matters are water, along with which condense the sulphide and carbonate of ammonium; besides this there is a dense black offensive viscid liquid, known as coal tar, which is a

very complex mixture, chiefly consisting of hydrocarbons and carbolic acid; some portions of these hydrocarbons supply the material from which aniline, the basis of most of the coal-tar dyes, is procured. The gaseous products are also very numerous; among them are olefiant gas, and some other gases of greater density, but of a similar character, which furnish the most important illuminating constituents; marsh gas, hydrogen, and carbonic oxide are also present; but they have little illuminating power. There are also small quantities of sulphuretted hydrogen, carbonic anhydride, cyanogen, and carbon disulphide, all of which it is the object of the gas-maker to remove. This is done by passing the gas over hydrated ferric oxide and slaked lime; the iron oxide removes the sulphuretted hydrogen and cyanogen, while the carbonic anhydride is stopped by the lime. The gas, when thus purified, is washed with water to get rid of small quantities of ammonia, and is afterwards stored up in vast iron reservoirs or gas-holders, from which it is distributed for consumption.

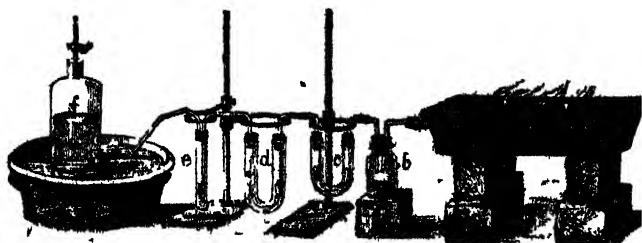
The removal of the sulphur compounds is especially necessary; because, when burned, they furnish sulphurous and sulphuric acids, which are very injurious to furniture, books, and paintings exposed to their action. The other materials furnish only water and carbonic anhydride, when burned with a sufficient supply of air.

Coal gas has a peculiar offensive odour, due in part to a compound of carbon and hydrogen called acetylene (C_2H_2). If coal gas escape into the atmosphere, it forms an explosive mixture. Hence, if a smell of gas be perceived in a room, no light must be admitted; the supply of gas should be at once shut off from the main, and the doors and windows thrown open to ventilate the house or the room. Afterwards the cause of the escape may be sought.

Exp. 206.—Place 15 or 20 grams of coal in small fragments in a tube of Bohemian glass, *a* (Fig. 67), 18 or 20 centimetres long, and sealed at one end; to the other end fit a good cork,

through which passes a quill tube bent at a right angle, and fitted into a phial (*g*). In one limb of the bent tube (*c*) place a piece of reddened litmus paper; in the other (*d*), a piece of filtering-paper moistened with a solution of lead acetate. Place a little limewater in the test-tube *e*, and collect the gas which comes over in a gas jar (*f*) provided with a stop-cock. Heat the tube *a* gradually by placing it in a tray of coarse wire gauze, and surrounding it with lighted charcoal; let it rise to

Fig. 67.



dull redness. Tar will become condensed, mixed with water in *b*, the red litmus in *c* will become blue from the ammonia, the lead salt will be blackened by the sulphuretted hydrogen, the lime-water rendered milky by the carbonic acid, while an inflammable gas will be collected in the jar, and may be burned by transferring the jar to the deep part of the trough, depressing it in the water, and lighting the gas as it escapes on gradually opening the stop-cock. Coke will be left in the glass tube.

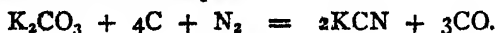
Exp. 207.—Hold a cold wide glass tube, of a metre or more in length, over a jet of burning coal gas: moisture will speedily become condensed on the cold sides of the tube, owing to the formation of water by the burning of the hydrogen.

Exp. 208.—Pour a little limewater into the tube, having closed one end with the hand after withdrawing it from the flame: the limewater will become turbid by absorbing carbonic acid.

A single jet of coal gas, consuming about 136 litres (5 cubic feet) of gas per hour, will produce nearly a quarter of a litre of water as it burns.

(41) CYANOGEN: *Symb.* Cn or Cy; *Rel. and Atom. Wt.* 26; *Mol. Wt.* 52; *Mol. Vol.* \square , Cy₂; *Sp. Gr.* 1·806.

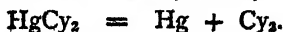
This is the name given to the compound which carbon forms with nitrogen, the 'blue producer,' owing to its being the characteristic component of Prussian blue. The two elements do not combine directly; but if nitrogen gas be passed over a red-hot mixture of charcoal and potassic carbonate, the carbon and nitrogen unite with the potassium, while carbonic oxide escapes—



Cyanogen is always one of the products obtained, in small quantities, during the distillation of pit coal; but its compounds are usually obtained from the cyanide of iron and potassium, which crystallises in large yellow tables, and is known as potassic ferrocyanide or prussiate of potash ($\text{K}_4\text{FeCy}_6, 3\text{H}_2\text{O}$).

This salt is prepared by heating to dull redness, in a covered iron pot, about 5 parts of parings of horns, hides, hoofs, or other animal refuse, with 2 parts of pearl ash and iron filings. The nitrogen and carbon combine at the high temperature, and unite with the iron and a portion of reduced potassium.

If this salt be dissolved in water and distilled with diluted sulphuric acid, the intensely poisonous prussic or hydrocyanic acid comes over, and the distilled liquid, if saturated with mercuric oxide, furnishes mercuric cyanide (HgCy_2); which, if thoroughly dried, and heated in a test-tube, becomes decomposed into metallic mercury and cyanogen gas—



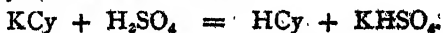
Cyanogen is a transparent, colourless gas, with a peculiar penetrating odour. It is very poisonous, and is combustible. If a jet of the gas be kindled, it burns with a characteristic rose-edged purple flame. It is soluble in water and in alcohol.

The peculiar character of cyanogen is its property, though a compound, of combining with the metals like one of the

halogens. Potassium when heated in the gas combines with it, and forms potassic cyanide. This circumstance has given rise to the theory of *compound radicals*,* now so extensively applied in organic chemistry, cyanogen being the first of these radicals which was obtained.

Cyanogen forms with hydrogen an acid compound—the intensely poisonous *hydrocyanic acid* (HCy), which, however, cannot be obtained by the direct union of its components. The vapour of this acid contains one volume of hydrogen and one of cyanogen, united without condensation, as in the case of hydrochloric acid, and the hydrogen acids of the other halogens. It is a very volatile liquid, which boils at 26.5° C.; but on account of its poisonous character, it is rarely prepared in a pure state. The vapour is inflammable, and burns with a whiter flame than that of cyanogen, which it resembles in appearance.

In a diluted state it is obtained by distilling a solution of the cyanide or of the ferrocyanide of potassium with diluted sulphuric acid, taking care that the vapours are carried away at once by a brisk current of air—

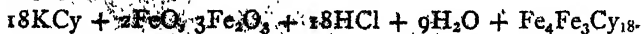


It is better not to make these experiments without the aid of some person of experience.

The solution of this acid has an odour resembling that of peach-blossoms. Its acid properties are feeble; it does not neutralise potash perfectly, but dissolves mercuric oxide very readily; and it gives a white precipitate of argentic cyanide (AgCy) when mixed with a solution of argentic nitrate. A good test of the acid is to add a slight excess of potash, and then a mixture of ferrous and ferric sulphate. A mixed precipitate of ferrous and ferric oxide is thus formed; and this,

* By the term radical is meant any substance which by uniting with a metal forms a salt, or with hydrogen forms an acid. In NaCl or common salt, chlorine is the simple radical; in HNO₃ or nitric acid, NO₃ or nitron is the compound radical. So in KCN or potassic cyanide, CN is the compound radical.

on adding hydrochloric acid in slight excess, to redissolve the excess of oxides of iron, leaves Prussian blue ($\text{Fe}_4\text{Fe}_3\text{Cy}_{18}$)—



Hydrocyanic acid, mixed with a peculiar essential oil, is obtained by distillation from the kernels of the bitter almond, and many kinds of stone fruit, after they have been crushed and mixed with water. The juice of the tapioca plant also contains it. It is also present in the water distilled off the leaves of the laurel, the peach, and several other shrubs.

Many cyanides of the common metals are insoluble in water, but are readily dissolved by solutions of the cyanide of potassium, or of sodium. The double cyanides thus obtained are numerous, and some of them very remarkable. The simple cyanides are intensely poisonous, and require great care in experimenting with them.

Exp. 209.—Dissolve 3 or 4 decigrams of potassic cyanide in about ten times their weight of water. Add a few drops to a small quantity of a solution of argentic nitrate in a test-tube. At first a copious white precipitate of argentic chloride will be formed—



and on further additions of the cyanide the precipitate will be gradually dissolved, AgCy , KC_7 being formed.

Exp. 210.—Melt 2 grams of potassic cyanide in a small iron spoon, and add a little litharge till the salt becomes slightly yellow. A bead of metallic lead will be formed, and the cyanide will have become converted into cyanate—



Potassic cyanide, in consequence of this tendency to absorb oxygen, is often used to reduce the metals from their oxides as a test in the laboratory.

Cyanogen forms a large number of other important compounds, but they are properly to be studied among the products of organic chemistry.

(42) *The Atomic theory.*—In the foregoing pages the terms *atom*, *atomic weight*, and *molecule* have been frequently

used. It will be necessary now to consider more exactly what these expressions mean.

Chemists assume that though every visible fragment of any elementary body admits of further division into a vast multitude of minute particles, there is a limit beyond which this process of subdivision cannot be carried by any known method, whether chemical or mechanical. These ultimate or indivisible particles are what are called the *atoms* of the element. No one has ever seen an atom, since such bodies are far more minute than the smallest fragments visible by the aid of our strongest magnifying glasses. The atoms of any particular element are further supposed to be exactly equal to each other in size and in weight; and when at the same temperature, to be absolutely similar one to another in all respects. But the atoms of any single element differ from those of all the other elements in chemical properties as well as in weight. Further, whenever chemical combination takes place between any two chemical elements, it is assumed that union occurs between their separate atoms. This chemical union is far more intimate than that effected by the force of cohesion which forms them into solids, still more than that mechanical mixture by which they are converted into masses or heaps of powder; and the difference between combination and mechanical mixture is that the atoms, being in the case of true combination held together by chemical force, cannot be separated by mechanical means; while such separation is practicable more or less completely when the two bodies are merely mixed mechanically, and therefore imperfectly, and often more or less irregularly.

These assumptions as to the atomic constitution of matter have been made with a view of explaining the quantitative laws which regulate chemical combination. This theory of the finite and definite divisibility of matter, or divisibility of matter down to a fixed limit, is in fact the only one hitherto conceived by which union in definite proportion is

192 *Law of Definite and Multiple Proportions, &c.*

accounted for; and if these suppositions be admitted, the known laws of chemical combination follow from them as a matter of necessity.

These laws are as follow:—

1. The law of definite proportions.—Whenever such combination occurs between two elements as to form any given compound, the proportions must be *definite*, since these proportions are determined by the relative weights of the atoms of the combining elements, and the atom cannot be subdivided.

2. The law of multiple proportions.—When the same pair of elements unite in several different proportions, these proportions must vary according to the terms of a *simple series of multiples*, since each atom of one element must unite with one, with two, or with three atoms of the other element, or in some other ratio almost equally simple, because the atom does not admit of subdivision.

3. The law of equivalent proportions.—Combination must also occur in *equivalent* proportions, since the amount of each element which is capable of displacing any of the other elements must be in the proportion of the weight of the atom of the displacing element, or of a simple multiple of that weight, and the atom cannot be subdivided.

4. The law of molecular weights.—In every compound body the *molecular weight*, or weight of the smallest particle of the compound which can exist, is necessarily that obtained by adding together the weights of all the atoms of the several elements which have united together to form the molecules of the compound body, since none of the atoms of the constituent elements can be subdivided.

Suppose, for example, that each atom of oxygen weigh 16 times as much as each separate atom of hydrogen; that the atom of chlorine weighs 35.5 times as much, the atom of nitrogen 14 times as much, the atom of bromine 80 times as much, the atom of silver 108 times as much, and the atom of mercury 200 times as much; exactly as is repre-

sented in the column headed 'Atomic Weights' in the table at page 192.

It follows that when chlorine and hydrogen unite to form hydrochloric acid, if one atom of each element enters into the formation of each molecule of the compound (HCl), hydrochloric acid must necessarily and invariably contain in every 36.5 parts by weight, whether it be grains, pounds, or tons, 1 part of hydrogen and 35.5 parts of chlorine.

In like manner, if each of the molecules of argentic bromide be formed by the union of 1 atom of silver with 1 of bromine (AgBr), then 188 parts by weight of this bromide will necessarily consist of 108 parts of silver and 80 of bromine.

Again, if each molecule of water consist of 2 atoms of hydrogen and 1 atom of oxygen (H_2O), it must happen that 18 parts by weight of water will always contain 2 parts by weight of hydrogen and 16 parts by weight of oxygen.

Suppose next that argentic bromide be heated in a stream of chlorine gas, the bromine will be displaced by the chlorine, and argentic chloride will be formed. Now if each molecule of argentic chloride (AgCl) be formed by the union of 1 atom of silver with 1 of chlorine, the bromine displaced must be in the proportion of 80 parts of bromine for every 35.5 of chlorine which unite with the silver; that is to say, 35.5 parts of chlorine are equivalent in combination to 80 parts of bromine.

It was at one time supposed that the chemical equivalent of the elements always represent the relative weights of their atoms, so that the term *atomic weight* was often used instead of that of *chemical equivalent*; but the two terms involve ideas which are essentially distinct. A simple substance can have but one atomic weight, but it may have two or more chemical equivalents; for instance, mercury forms two compounds with chlorine, viz. calomel and corrosive sublimate. In calomel 300 grains of mercury are combined with 35.5 grains of chlorine; whilst in corrosive sublimate

the 200 of mercury are united with 71 grams of chlorine, or twice as much; and this is explained upon the supposition that the atom of mercury is in calomel united with 1 atom of chlorine (HgCl), whilst in corrosive sublimate it is united with 2 atoms (HgCl_2). But if we compare the quantity of mercury in each compound with the same weight, 35.5, of chlorine, we find in calomel that 200 parts of mercury are equivalent to 35.5 parts of chlorine; whilst in corrosive sublimate 100 parts of mercury are equivalent to the same 35.5 parts of chlorine; consequently mercury has two different equivalents in the two compounds.

Again, in the five oxides of nitrogen we have an excellent example of multiple proportion. If 2 atoms of nitrogen are supposed in each case to be concerned, we find the composition of each represented by the following numbers: nitrous oxide contains in every 44 parts 28 parts of nitrogen and 16 of oxygen, or 2 atoms of nitrogen and 1 of oxygen; nitric oxide in every 60 parts contains 28 parts of nitrogen and 32 of oxygen, or 2 atoms of nitrogen and 2 of oxygen; nitrous anhydride in every 76 parts contains 28 of nitrogen and 48 of oxygen, or 2 atoms of nitrogen and 3 of oxygen; nitrogen peroxide in every 92 parts contains 28 of nitrogen and 64 of oxygen, or 2 atoms of nitrogen and 4 of oxygen; while nitric anhydride in every 108 parts contains 28 of nitrogen and 80 of oxygen, or 2 atoms of nitrogen and 5 of oxygen; the series being represented as N_2O , N_2O_2 , N_2O_3 , N_2O_4 , and N_2O_5 .

It has been ascertained that equal measures or volumes of every gas and every vapour taken at a sufficient distance from its boiling point, no matter whether simple or compound, expand equally for an equal rise of temperature, if both are compared under equal pressures, and at the same temperatures. It is also true that all gases and vapours expand or contract equally when equal volumes of the different gases are submitted, at the same temperatures, to an equal diminution or increase of pressure. Hence it

appears to be a necessary conclusion that equal volumes of all gases contain an equal number of molecules, whether those molecules be simple or compound. Further, the molecules of the same substance are all absolutely similar to each other in size, weight, and chemical properties, if compared under similar circumstances.

The term *molecular volume* is used to signify the space occupied by a molecule of the body in the form of gas or vapour, compared with that of the atom of hydrogen, or the *atomic volume* of hydrogen. Now the volume of the molecule of a compound body in the aeriform state $\boxed{\text{H}_2\text{O}}$ is exactly double the volume of the atom of hydrogen $\boxed{\text{H}}$.

The *atom* is defined to be the smallest and chemically indivisible particle of each element which can exist in a compound, united with other particles, either of the same or of different elements, but which is not known in a separate form; and the *molecule* of an element is defined to be the smallest quantity of that elementary substance supposed to be capable of existing in a separate form. If H, for instance, represent the atom of hydrogen, H₂ will represent its molecule. Each molecule of chlorine and of the other allied elements when in the gaseous state appear, for reasons to be explained immediately, to consist of two atoms. When a molecule of hydrogen is made to react chemically upon a molecule of chlorine, two molecules of hydrochloric acid are formed, the half molecule of hydrogen exchanging places with the half molecule of chlorine—



It will be desirable to develop these considerations a little more fully. The number adopted for the atomic weight of any element is based upon a careful chemical analysis of several compounds of that element. Suppose, for example, the atomic weight of copper to be the subject of experiment, and that a quantity of the pure oxide of the metal has been prepared, and a portion carefully weighed, and heated in

a stream of pure hydrogen gas. The hydrogen gradually removes all the oxygen in the form of steam, leaving nothing but pure copper behind. On weighing this copper, the quantity of oxygen originally combined with it in the oxide is ascertained by the loss of weight experienced. Then the relative proportions between the combining proportion of copper and oxygen, referred to hydrogen as the unit, can be easily calculated.

But this determination would not be sufficient to settle the atomic weight if taken alone, even if other analyses of this same oxide and of other compounds of copper gave results which showed that the experiments had been made with exactness. It is necessary also to know the number of atoms in the molecule of the different compounds of the substances analysed; whether, for instance, the number of atoms of copper in the molecule of its oxide be one of copper to one of oxygen, two of copper to one of oxygen, or two of oxygen to one of copper, two of copper to three of oxygen, or any other proportion. In the case of solid bodies, not convertible easily into vapour, the determination is often attended with difficulty and uncertainty. There are, however, various considerations by which this conclusion may be arrived at with more or less probability. One of the best methods consists in comparing together all the compounds of the element under examination, for the purpose of finding out the smallest proportion in which that element enters into any compound molecule, for this must represent its atom, by the definition of the word which we have adopted.

In cases where bodies can be converted into vapour, this task is much facilitated by the very circumstance. For example, a large number of thousands of hydrogen have been analysed. Most of them may be obtained in the form of gaseous vapour; in which case their specific gravities in the aeriform condition may be ascertained by experiment. From these specific gravities the relative weights, or weights com-

pared with that of an equal bulk of hydrogen, and the molecular weights are at once easily obtained.

Some of the more important of these compounds have been already described, and they are mentioned in the following list.

Compounds of Hydrogen	Molecular Volume	Weights referred to Hydrogen	Weights of Hydrogen in Molecule
Hydrochloric Acid . . .	<input type="text"/>	36.5	1
Hydrobromic Acid . . .	<input type="text"/>	81.0	1
Hydrogen Gas . . .	<input type="text"/>	2.0	2
Water . . .	<input type="text"/>	18.0	2
Sulphuretted Hydrogen . .	<input type="text"/>	34.0	2
Ammonia . . .	<input type="text"/>	17.0	3
Phosphuretted Hydrogen . .	<input type="text"/>	34.0	3
Ofosant Gas . . .	<input type="text"/>	28.0	4
Marsh Gas . . .	<input type="text"/>	16.0	4

Now if the molecule of hydrogen weigh 2, the smallest weight of hydrogen which is contained in an equal volume of vapour of any of the compounds of hydrogen in the list, and it may be added in any others that are known, is half that amount, or 1. Hence chemists have concluded that this quantity of hydrogen is the smallest that can enter into combination, or, according to the supposition with which we began, that it is to be regarded as the atom of hydrogen. Now hydrogen has the smallest combining number of any element known, so that it has been found convenient to take the hydrogen number as 1, or the unit of the scale, with which the atomic weights of all the other elements are compared, as has been done in the table given at page 198, so

that supposing the weight of the atom of hydrogen to be known, the *atomic weight* of any other element would be the number which represents how many times this atom is heavier than the atom of hydrogen.

The following table contains a list of such of the elementary bodies as have been converted into vapour in such a manner as to admit of determining their specific gravity in that form, and thus of ascertaining the number of atoms in the molecule, on the supposition that equal volumes of every gas or vapour contain an equal number of molecules:—

Element	Atomic Weights	Weights of equal Volumes of Vapour	Atoms in a Molecule	Specific Gravity of Vapour	
				Observed	Calculated
Cadmium . . .	112	56	1	3.94	3.8690
Zinc . . .	65	32.5	1		
Mercury . . .	200	100	1	6.976	6.9101
Hydrogen . . .	1	1	2	0.0692	0.0691
Chlorine . . .	35.5	35.5	2	2.47	2.4531
Bromine . . .	80	80	2	5.54	5.5281
Iodine . . .	127	127	2	8.716	8.7560
Oxygen . . .	16	16	2	1.1056	1.1056
Sulphur . . .	32	32	2	2.23	2.2168
Selenium . . .	79.5	79.5	2	5.68	5.4681
Tellurium . . .	129	129	2	9.00	9.0130
Nitrogen . . .	14	14	2	0.9713	0.9714
Phosphorus . . .	31	62	4	4.42	4.2840
Arsenicum . . .	75	150	4	10.60	10.1670

CHAPTER XI.

B. THE METALS.

(43) *The Metals in General.*—There is no absolute distinction between the non-metals and the metals, but the subdivision is practically convenient, and it is usual to consider a body which has a high lustre, great opacity, and is a

good conductor of heat and electricity, as a metal. But on the one hand, graphite, although it has all these properties, is not reckoned amongst the metals; and on the other, arsenicum and tellurium, though possessing them, are by some chemists considered as non-metals.

The metals differ very much in chemical properties; some, like potassium and sodium, have an intense attraction for oxygen, whilst others, like gold and silver, have but a feeble attraction for it. As a rule, the lighter metals are those which are most easily oxidized. In the following table the lightest metals are placed first. The metals exhibit a very great variation in density. Three of them are light enough to float in water, and lithium is lighter than any known liquid, while platinum is the heaviest of all known substances.

SPECIFIC GRAVITIES AND FUSING POINTS OF METALS.

	Specific Gravity	Fusing Point		Specific Gravity	Fusing Point
Lithium .	0.593	180°	Molybdenum .	8.62	
Potassium .	0.865	62.5	Nickel .	8.82	
Sodium .	0.972	97.6	Copper .	8.95	1090°
Rubidium .	1.52	38.5	Cobalt .	8.95	
Caesium .	1.578		Bismuth .	9.80	264
Barium .	1.743		Silver .	10.53	1023
Strontium .	2.1		Lead .	11.36	325
Aluminum .	2.54		Ruthenium .	11.4	
Arsenicum .	2.67		Palladium .	11.6	
Tellurium .	5.95		Thallium .	11.9	294
Antimony .	6.25		Rhodium .	12.1	
Chromium .	6.71	450	Mercury .	13.596	-39
Zinc . . .	6.81		Tungsten .	17.6	
Tin . . .	7.15	412	Uranium .	18.4	
Iron . . .	7.29	228	Gold . . .	19.34	1102
Manganese .	7.84		Iridium . .	21.15	
Cadmium .	8.01		Osmium . .	21.4	
	8.69	228	Platinum .	21.5	

The melting points of the metals vary widely. In the table the melting points of all the metals, so far as they have been ascertained, are given. Mercury is liquid at all

ordinary temperatures; potassium and sodium melt beneath the boiling point of water. Zinc melts below, and copper above, a red heat; silver, gold, and copper require a very bright red heat to fuse them. Cast iron melts at about 1500° , and wrought iron not lower than 1800° C. Cobalt, nickel, and wrought iron require the strongest heat of the forge to melt them. Molybdenum, chromium, tungsten, and palladium do not completely melt even at this temperature; and platinum, rhodium, indium, vanadium, ruthenium, and osmium cannot be melted but in the heat of the oxy-hydrogen blowpipe, or that of the voltaic arc.

Some few of the metals may be converted into vapour readily, and are ordinarily purified by distillation. Mercury, arsenicum, tellurium, cadmium, zinc, magnesium, potassium, sodium, and rubidium are thus purified. Mercury boils at 350° C. Arsenicum is volatilised below redness. Cadmium requires a full red heat (860°), at which point it boils, and may be distilled; and the boiling point of zinc, though as high as 1040° , is equally fixed. Potassium, sodium, magnesium, and rubidium require a still higher temperature, which has not been measured.

Many of the other metals including silver and gold, may be volatilised by the intense heat of the sun's rays when brought to a focus by a very large convex lens.

Several of the metals when rubbed give out a characteristic odour, as is the case with iron, tin, and copper. Arsenicum, when volatilised, emits a strong odour of garlic. The taste of many of the soluble salts of the metals is astringent or acrid, and of the peculiar kind termed metallic.

The most usual colour exhibited by the metals is a white, of varying shades. It is nearly pure in silver, platinum, cadmium, and magnesium; yellowish in tin; bluish in zinc and lead; grey in iron and arsenicum; and is reddish in bismuth. Calcium is pale yellow, gold full yellow; and copper is red.

Many of the metals show the properties of *malleability*, or the power of being flattened under the hammer. They may also be extended into ribbon or *foil*, by passing them between steel rollers: among these are gold, silver, platinum, palladium, copper, iron, aluminium, tin, lead, zinc, and thallium. Gold is the most malleable of the metals, but silver and copper may also be hammered into very thin leaves. The same metals are likewise *ductile*; that is, they admit of being drawn into wire, often finer than a hair, by drawing them through holes in a hard steel plate, termed a draw plate, the holes through which the wire is made to pass being successively smaller and smaller.

On the other hand, there are metals so brittle that they may be powdered without difficulty: such are arsenicum, antimony, and bismuth. These metals have a crystalline structure, and are very hard. Metals which have a fibrous texture, like bar iron, are, on the contrary, very tough.

When the metals are combined with each other, the resulting substance is called an *alloy*. Many of these, such as brass, German silver, bronze, and pewter, are used largely in the arts, on account of advantages which they offer over their constituent metals in increased hardness and elasticity, as well as increased fusibility. Brass is a hard, somewhat fusible alloy, consisting of about two-thirds of copper and one-third of zinc. If brass be melted with about a sixth of its weight of nickel, it furnishes German silver. Bronze is an alloy of tin and copper, of which there are several varieties: with 10 per cent. of tin it forms the tough gun-metal, with 20 per cent. of tin it furnishes the sonorous, elastic bell-metal; and with 33 per cent. of tin the hard, white, brittle metal used for the mirrors of telescopes.

The white metal used in types for printing is an alloy of about 1 part of antimony, 1 of tin, and 2 of lead; it is fusible, expands on becoming solid, so as to fill the mould, and is hard enough to bear pressure, but will not cut the paper. All the alloys melt at a lower temperature than

that which would be the mean of the fusing points of their components.

Exp. 211.—Heat in a small iron ladle 20 grams of lead; as soon as it is melted add 40 grams of bismuth and 10 of tin; they will fuse quickly, and an alloy will be thus obtained known as *fusible metal*: it melts when thrown into boiling water, although tin, the most fusible of its components, does not melt below 228°C .

A combination of a metal with mercury forms an *amalgam*. Some amalgams are soft and semi-solid; others are brittle and crystalline. Alloys and amalgams appear to consist of definite compounds, which are often mixed with, or dissolved by, an excess of one of the metals employed; for the proportion of the metals used in an alloy can be varied within any limits.

Some few of the metals are found in the *native*, or uncombined, state in the earth. Among these the most important are gold, silver, platinum and a few rare metals which accompany it, mercury, bismuth, and copper. More usually the metals occur united with sulphur, when they preserve their metallic brilliancy, but not their ductility or tenacity. Lead, antimony, mercury, copper, iron, and zinc are often, and some of them almost always, found in the condition of sulphides. Other metals—such, for instance, as tin, iron, manganese, and chromium—are met with as oxides, under the aspect of dull blackish or earthy bodies. The metals of the earths, and of the alkalis, are generally found in the form of salts, such as sulphates, carbonates, silicates, or chlorides. Further particulars respecting the *ores* of the metals, their distribution over the surface of the earth, the formation of mineral veins, and the methods employed for extracting the metals for use in the arts, will be found in the text-book on ‘Metallurgy.’

144. Classification of the Metals.—The metals may be divided into 10 groups, founded upon their different degrees of attraction for oxygen, and the properties of the oxides which they form.

Group 1 : 5 Metals of the Alkalies, viz. 1. Cæsium ; 2. Rubidium ; 3. Potassium ; 4. Sodium ; and 5. Lithium, with which it is convenient to arrange the salts of ammonium, although it is not a simple body.—These metals are monads, and displace 1 atom of hydrogen from the radicals of the acids. They are soft, easily fusible, and volatile at high temperatures. They have an intense attraction for oxygen, and become tarnished as soon as they are exposed to the air. They decompose water instantly at all temperatures, with rapid disengagement of hydrogen, and form a soluble, powerfully caustic and alkaline compound, which may be regarded as water in which half the hydrogen is replaced by metal. They form but one set of salts with the halogens. Though they furnish but a single chloride, they yield several sulphides, all of which are soluble. When exposed to the air their oxides absorb carbonic acid greedily, and form soluble carbonates. Only two of them, potassium and sodium, are sufficiently abundant to require description. Cæsium and rubidium are of quite recent discovery, and were found in minute quantity in the water of a mineral spring, of which the saline residue was submitted to examination by the method of spectrum analysis, lately discovered, and they have since been found in minute quantity in the ash of various plants, and in some crystallised minerals.

Group 2 : 3 Metals of the Alkaline Earths, viz. 1. Barium ; 2. Strontium ; and 3. Calcium.—These are dyads ; they displace two atoms of hydrogen from the radicals of the acids. When thrown into water they decompose it with avidity, and set hydrogen free. They form powerfully basic oxides, which are soluble in water, though lime is only sparingly so. These oxides absorb carbonic acid rapidly, and form carbonates which are insoluble in water, but somewhat soluble in a solution of carbonic acid. Their phosphates are insoluble in water.

Group 3 : Metals of the Earths.—The only one of practical importance is 1. Aluminum ; but 2. Glucinum ; 3.

Yttrium; 4. Erbium; 5. Cerium; 6. Lanthanum; and 7. Didymium, are commonly included in this division. The last six are, however, very rarely met with, and their properties are only imperfectly known.

Aluminium is a triad: it forms but one oxide; this is insoluble in water, and is but feebly basic.

Group 4: 4 Magnesian Metals, viz. 1. Magnesium; 2. Zinc; 3. Cadmium; 4. Indium.—These metals are dyads; they form but a single oxide, which is insoluble in water. They decompose steam at a red heat, but are without action on water at common temperatures. They form a single soluble chloride, and a single nearly insoluble sulphide.

Group 5: 6 Metals allied to Iron, viz. 1. Cobalt; 2. Nickel; 3. Uranium; 4. Iron; 5. Chromium; and 6. Manganese.—These metals are remarkable as forming two sets of compounds, in one of which the metal is dyad, in the other triad. They furnish several oxides: those which contain least oxygen are basic and insoluble; those which contain most are often soluble, and are then distinctly acid. Several of these metals are magnetic; they are oxidized by passing steam over them when heated to redness, though they do not decompose water at ordinary temperatures.

Group 6: 4 Metals allied to Tin, viz. 1. Titanium; 2. Tin; 3. Zirconium; and 4. Thorium.—They are all tetrad, or equivalent to 4 atoms of hydrogen. Tin is the only one of practical importance: it furnishes two oxides, both capable of acting as bases; but the higher oxide is more often acid.

Group 7: 2 Metals, Molybdenum and Tungsten, which are hexad, or equivalent to 6 atoms of hydrogen.—They yield trioxides, which furnish metallic acids; but we shall not enter into any description of them.

Group 8: 6 Metals. They present in their combinations an analogy with phosphorus, viz. 1. Niobium; 2. Tantalum; 3. Vanadium; 4. Arsenium; 5. Antimony; and 6. Bismuth.—They furnish at least two oxides. We shall not enter further

into any description of the first three of these metals, but the last are of practical importance.

Group 9: 3 Metals, viz. 1. Copper; 2. Lead; and 3. Thallium, which are not closely related.

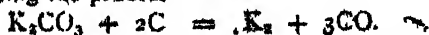
Group 10: 4 noble Metals, viz. 1. Mercury; 2. Silver; 3. Gold; 4. Platinum, with which are associated 5 other rare metals, viz. 5. Palladium, 6. Rhodium; 7. Ruthenium; 8. Osmium; and 9. Iridium, which we need not further notice.—The first four metals form more than one oxide, but have so slight a tendency to unite with oxygen that their oxides are decomposed by exposure to a heat below redness. All the metals of this group are commonly found in the native state; but mercury and silver also occur as sulphides. Their attractions both for chlorine and for sulphur are much stronger than for oxygen. Each forms more than one chloride, their compounds have a tendency to combine with the chlorides of the alkali-metals to form double salts.

GROUP I.—METALS OF THE ALKALIES.

1 POTASSIUM 2 SODIUM. 3 LITHIUM. 4 CESIUM.
5 RUBIDIUM — (AMMONIUM).

(45) POTASSIUM: *Symb* K; *Atom. Wt.* 39; *Sp. Gr.* 0.865, *Fusing Pt.* 62.5°.

This metal was originally obtained by decomposing a fragment of caustic potash by means of a powerful voltaic battery, when globules of potassium were separated at the negative wire. It is now prepared by distilling potassic carbonate mixed with charcoal, at an intense heat, in iron bottles, and condensing the green vapours of potassium in receivers containing naphtha, carbonic oxide being disengaged during the process—

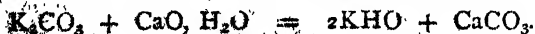


This is a difficult and dangerous operation. Potassium vapour takes fire instantly in the air or on contact with water; it also absorbs carbonic oxide, and the compound thus formed, if kept, gradually becomes changed into a black, powerfully

explosive compound. To avoid this danger potassium is always redistilled, immediately after its preparation, in a small iron retort containing naphtha vapour.

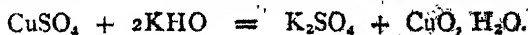
Potassium is a brilliant silver-white metal, soft enough to be spread with a knife. It tarnishes immediately that it is exposed to the air, and decomposes water, evolving hydrogen as soon as it is thrown into the liquid. (Exp. 30.) The gas takes fire from the heat produced by the action. It is necessary to preserve the metal either in vessels closed so as to prevent access of air, or under some liquid, such as naphtha, which contains no oxygen. It combines immediately with chlorine, bromine, iodine, and sulphur, if heated with them.

Potassium furnishes an important basic oxide (K_2O), potash; besides this, there are two other oxides (K_2O_2 and K_2O_4), which, when thrown into water, give off oxygen, and furnish a solution of potash. The anhydrous potash is difficult to obtain pure, and is seldom prepared; but its hydrate is a very important substance, and is known as caustic potash, or *potassic hydrate* (KHO). This, when dissolved in water, furnishes potash ley. It is prepared by mixing a solution of potassic carbonate with slaked lime—



If the solution is poured off from the calcic carbonate and evaporated down in a silver dish, an intensely caustic solid substance is left, which fuses at a red heat, and may be cast into metallic moulds. It furnishes the hydrate of potash. This substance absorbs both moisture and carbonic acid from the air. Caustic potash, if fused in glass or porcelain dishes, corrodes and dissolves them. It also attacks platinum vessels, but has little action on silver. It is very soluble both in water and in alcohol. The solution decomposes the fats and oils, and converts them into soluble soaps. Ordinary soft soap contains potash as its base. Caustic potash is also a valuable agent in the laboratory, where it is used for the

purpose of absorbing acid gases, such as the carbonic. In consequence of its powerful attraction for acids, it readily decomposes the salts of all metals which form oxides insoluble in water, and it precipitates the oxide of the metal in the form of hydrate, while the radical of the acid forms a potassic salt, which remains in solution; such a salt, for example, as the cupric sulphate is decomposed as follows:—



Potash is found in all fertile soils, generally in the clay derived from the felspar, which, after crumbling down, has become mingled with other substances. Growing plants require potash to aid in forming their tissues. The alkaline salt is dissolved by the rain-water from the soil, absorbed by the roots, and carried by the circulation of the sap into the plant, where it becomes combined with the radical of some vegetable acid. When the plant is burned the salt of the vegetable acid is decomposed, and the potassium remains in the ash, chiefly in the form of carbonate. The more soluble portions of this ash are washed out by the action of water, which when evaporated leaves the potassic carbonate, or *potash*, of commerce, which is imported largely from North America and Russia. *Pearlash* is the first produce, refined by a second solution in a very small quantity of water, and evaporation to dryness.

Potassic chloride has also been found native, in considerable amount, in the salt beds of Stassfurth, near Magdeburg; and it is present in sea water in quantity sufficient to render this a very important source of supply.

Potassium forms five sulphides: K_2S , K_2S_2 , K_2S_3 , K_2S_4 , and K_2S_5 . They are all soluble, and have a strongly alkaline reaction. When mixed with an acid, they all give off sulphuretted hydrogen, and also, except in the case of K_2S , deposit sulphur.

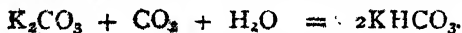
Potassic Carbonate (K_2CO_3) is a very soluble salt, which, if exposed to the air, attracts moisture from it, and soon

becomes liquid. It is strongly alkaline, and restores the blue colour of red litmus paper.

Exp. 212.—Burn some dry brushwood; collect the ash, and wash it with five or six times its bulk of water. Filter off from the undissolved substances. Test the solution with a piece of reddened litmus paper, which will at once become blue. Evaporate the solution to dryness in a small porcelain dish. If the dry mass be left exposed to the air for a few hours it will become moist. The potassic carbonate, of which it chiefly consists, attracts moisture rapidly and deliquesces. To a portion of the salt add a few drops of hydrochloric acid: brisk effervescence occurs.

Exp. 213.—Place 30 grams of pearlash in a half-litre bottle, and dissolve it in 250 c. c. of water. Shake 20 grams of quick lime with five or six times its bulk of boiling water, and add the pasty mixture (about 120 c. c. in bulk) to the solution of pearlash. Agitate the mixture, and let it stand till it is clear. Pour off a portion of the liquid: it is a solution of caustic potash. Add to it some hydrochloric acid: no effervescence will occur. Agitate a tablespoonful of olive oil in a small phial with 3 or 4 c. c. of the caustic solution diluted with ten times its bulk of water: a milky-looking liquid will be formed, which is the first stage in the making of soap.

Potassic Hydric Carbonate (KHCO_3).—If a current of carbonic acid gas be passed through a strong solution of potassic carbonate, it is quickly absorbed, and crystals of a less soluble salt, often called the *bicarbonate*, are formed—



Potassic Nitrate (KNO_3).—Another important salt, usually called *nitre* or *saltpetre*, is found on the surface of the soil in some parts of tropical India. It is also obtained in temperate climates by allowing animal matter mixed with lime rubbish to decay in heaps, which are moistened from time to time, and from which the nitre is at intervals removed by washing. The nitrogen in the animal refuse becomes slowly oxidized into nitric acid, and this combines with the lime and potash present.

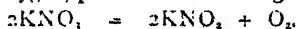
Nitre has a cooling saline taste, and is soluble in about $3\frac{1}{2}$ times its weight of cold water.

Exp. 214.—Dissolve 150 grams of nitre in a quarter of a litre of boiling water, and allow it to cool slowly: six-sided prisms of nitre will crystallise from the liquid.

Exp. 215.—Mix a portion of the solution with three or four times its bulk of water, and dip some strips of filtering-paper into the liquid. When dry the paper, called *touch paper*, will smoulder if kindled.

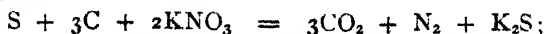
Exp. 216.—Throw a little nitre into a clear fire: the embers will burn with brilliant sparks.

Exp. 217.—Put a few dry crystals of nitre into a test-tube, and heat them over a lamp: they will melt to a clear liquid. Heat them more strongly: they will be decomposed, gas will escape, which will rekindle a glowing match, and which at first consists of pure oxygen, potassic nitrite being formed—



The principal use of nitre depends upon this readiness to put with oxygen, of which it contains nearly 48 per cent., and which enables it to add great intensity to combustion.

Gunpowder is a mechanical mixture of about 75 parts of nitre, 15 of charcoal, and 10 of sulphur; the quantities of the ingredients used being nearly in the proportions of 1 atom of sulphur, 2 of nitre, and 3 of charcoal. An excess of sulphur is to be avoided, as it corrodes the gun. The application of a spark, or even of a temperature of about 250°C. , produces an instantaneous decomposition of the mixture, attended with an immense production of gas (chiefly carbonic anhydride and nitrogen) at a very high temperature, so that the gases at the moment of firing become expanded to at least 1500 times the bulk of the gunpowder. The chemical change is sometimes roughly represented as follows:—



though it is really much more complex. Gunpowder thus* contains within itself the oxygen necessary to enable it to burn in a space excluded from air, or even under water; the

oxygen forming either carbonic oxide or carbonic anhydride, while nitrogen is set free, and the sulphur remains combined with the potassium.

(46) **a. SODIUM:** *Symb.* Na; *Atomic Wt.* 23; *Sp. Gr.* 0.972; *Fusing Pt.* 97.6°.

Sodium much resembles potassium. It is obtained from its carbonate, by heating it with charcoal, in a similar way to that followed with potassium, but it is more easily managed. It is made in large quantities as a preparatory process in the extraction of aluminum and magnesium. Sodium gives off a colourless vapour, which burns with a bright yellow flame. When thrown into water it rises to the surface, and disengages hydrogen freely; but the gas does not generally take fire unless the water is heated first, or is small in quantity.

Common salt, sodic chloride (NaCl), is the great source from which all compounds of sodium are obtained. This is met with in large quantities in sea water, which contains more than a quarter of a pound in a gallon, or about 27 parts in 1000. It is also found in extensive deposits in Cheshire, and still more abundantly in the mines of Wielitzka, in Poland. Sodium is also found in Atacama as nitrate, and in many rocks and minerals, as, for instance, in soda felspar or albite, and in cryolite ($3\text{NaF}, \text{AlF}_3$), a fluoride of sodium and aluminum.

Sodium forms two oxides, Na_2O and Na_2O_2 . The first is the only one of importance. It is the base from which the salts of sodium are derived, but is seldom obtained in a pure state.

Caustic Soda, or *sodic hydrate* (NaHO), is a white solid, very soluble in water. Caustic soda is formed on a large scale in the alkali works, but it is easily prepared by treating a solution of sodic carbonate with slaked lime, in a manner similar to that directed for obtaining caustic potash, which it

closely resembles. Soda ley, or the solution of this hydrate in water, is largely used in the manufacture of ordinary hard soaps.

Sodic Chloride, or common sea salt (NaCl), is often obtained from sea water, by allowing it to flow into very shallow pools—constructed for the purpose, and called salt pans, or salterns—where the water evaporates, and becomes concentrated in the heat of the sun. The salt crystallises out in cubes, and forms the *bay salt* of commerce. The mother liquor, or bittern, retains salts of potassium and magnesium, which are extracted; and it also furnishes the principal source of bromine. In some inland countries brine springs furnish important sources of supply of this chloride. Vast beds of *rock salt* also occur in several countries, as in Galicia, Canada, Spain, and in several parts of the British Islands, especially in Cheshire. It is a common practice where coal is cheap to allow water to flow down into the bed of salt, and to pump up the liquor when it has become saturated. The brine is then boiled down and crystallised. Our common table salt is obtained in this way.

Sodic chloride in small quantities is essential to life. It is soluble in less than three times its weight of water. When heated suddenly it decrepitates, and may be melted at a bright red heat. Fish and meat are often salted to preserve them from putrefaction; but when so prepared they are much less nutritious than when fresh, as the salt extracts the nutritive and flavouring juices, which become saturated with it and form *brine*. Salt is used largely as a manure to land. It is consumed in immense quantities in the alkali works for preparing other compounds of sodium; and it furnishes the supply of chlorine and hydrochloric acid.

Sodic Sulphate ($\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$) was formerly known as Glauber's salt. It crystallises in four-sided prisms, which crumble down to a white powder, and lose their water when exposed to the air. It is very soluble in water, but more so at 33°C . than either at a higher or lower temperature. *Salt*

cake is the name given to the sulphate when prepared by decomposing common salt in a furnace with sulphuric acid, at a high temperature, as a preliminary in the manufacture of soda ash. Immense volumes of hydrochloric acid gas are then given off, and these are condensed by causing the fumes to pass through large towers filled with broken coke or stone, over which a stream of water is kept constantly trickling. A solution of hydrochloric acid is thus obtained, while the sodic sulphate is left in the furnace. The decomposition occurs in two stages; in the first, one half only of the salt is decomposed, hydric sodic sulphate being formed, and the first half of the hydrochloric acid comes off easily. The expulsion of the last half of the acid requires a higher temperature, and is driven off by the action of the fusible hydric sodic sulphate on the other half of the sodic chloride—



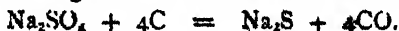
Sodic Carbonate ($\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$).—This salt crystallises in large transparent prisms, which effloresce in the air. It has a soapy disagreeable taste, and restores the blue colour to reddened litmus paper. It is very soluble in water; and when heated melts in its water of crystallisation, which amounts to 63 per cent. of the salt. The dried residue melts at a bright red heat. The dry salt is made in enormous quantities, and sold as *soda-ash*, which is used in the manufacture of glass, in soap-making, in cleansing calicoes, and for a variety of other important purposes. In order to prepare this carbonate, salt cake is mixed with about its own weight of chalk and rather more than half its weight of coal dust. This material is then thrown in charges of about 125 kilog. upon the floor of a hot, reverberatory furnace (Fig. 69), divided into two beds: on the more distant bed (b) it is first heated, and then thrust on to the bed a, nearest the fire (c). There it melts, and gives off jets of gas, which take fire, and burn with a yellow flame. As soon as this escape of gas ceases, the

mixture is raked out into an iron trough, the next charge is pushed down to the lower bed, and a fresh charge is introduced. The chemical change which occurs in this fusion

Fig. 69.



consists mainly: 1st, in reducing the sodic sulphate to sulphide, while carbonic oxide is formed and escapes, taking fire, and becoming converted into carbonic anhydride—



2nd. The sodic sulphide is immediately decomposed by the chalk into calcic sulphide and sodic carbonate—



This sodic carbonate is always mixed in the process with quicklime, as it is found necessary to employ chalk in excess, and this chalk becomes lime in the high temperature of the furnace. A certain quantity of coal is also always used in excess, and this likewise remains mixed in the fused mass, technically known as *ball soda* or *black ash*.

This ball soda is now broken up, and placed in water at about 45° C., which dissolves out the sodic carbonate, but leaves the calcic sulphide undissolved. This undissolved residue is the soda waste, so troublesome to the manufacturers. The solution of soda is next evaporated down, and when calcined furnishes the *soda-ash* or crude alkali of commerce, which contains from 50 to 56 per cent. of caustic soda (Na_2O), in the form of carbonate and hydrate. If this soda-ash be dissolved in water, and the liquid allowed to cool slowly in a tank, beautiful transparent crystals of the carbonate (*soda crystals*) are gradually formed.

Hydric Sodii Carbonate (NaHCO_3), often called bicarbonate, is obtained by saturating a solution of the carbonate with carbonic acid. It is deposited in white crystalline grains, and is the substance commonly used for producing an effervescing drink with lemon juice.

Tests for the Alkali Metals in Combination.—The salts of potassium are easily distinguished from those of sodium.

Exp. 218.—To a pretty strong solution of the salt in question add a solution of tartaric acid, and stir the mixture with a glass rod. If potassium be present, white gritty crystals of cream of tartar ($\text{KHC}_4\text{H}_4\text{O}_6$) will be deposited, but no such precipitate will occur with salts of sodium.

Sodium forms salts all of which are soluble in water, so that it does not produce any precipitate with ordinary test solutions. It also gives a yellow colour to a colourless flame, such as that of a spirit lamp or a Bunsen gas burner, whereas potassium gives a violet-coloured flame.

The alkalies are all well distinguished from each other by the colour which they give to flame, especially if the flame be examined by means of the spectroscope. Potassium is then recognised by a single line in the red and another in the violet; sodium, by a pair of intense lines, so close that they generally seem but one, in the yellow; lithium, by a single intense crimson line, and sometimes a faint one in the orange if the flame be of a very high temperature; rubidium, by two lines in the red and two in the blue; and caesium by two intense lines in not so far on the blue as those of rubidium, though in these two last-mentioned spectra there are other lines of less importance.

Potassium salts may further be distinguished from sodium by means of platinic chloride, which forms with the chlorides of both metals a double salt; that with potassium (2KCl , PtCl_4) is nearly insoluble, that with sodium (2NaCl , PtCl_4 , $4\text{H}_2\text{O}$) crystallises in long soluble needles.

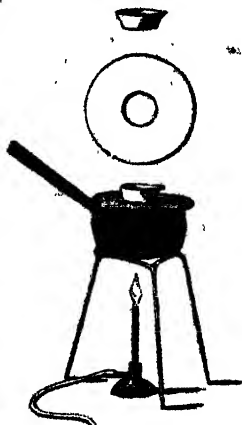
Exp. 219.—Add to the solution two or three decigrams of potassium chloride in a small porcelain dish, a few drops of hydro-

chloric acid, then an excess of solution of platinic chloride; evaporate to dryness over a saucepan of boiling water, arranged so as to form a water-bath, a circular disk of tin, large enough to project a little way beyond the edge of the saucepan, being substituted for its lid, and a circular hole a little smaller than the dish having been made in this lid, as shown in Fig. 70. When cold, the residue is to be re-dissolved in a few drops of water, which will remove the soluble materials, and leave the sparingly soluble salt of platinum and potassium in small octahedra.

Cæsium and rubidium also form similar double chlorides with platinum chloride, but they are much less soluble in hot water than the potassium salt, a difference which is sometimes made use of to separate these bases from potassium.

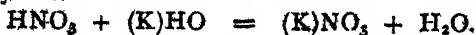
(47) 3. *Ammonium* (H_4N).—This is not a metal, nor is it even known in a separate form; but it is generally considered to be the compound *quasi* metal contained in the salts formed by the action of the volatile alkali ammonia on the acids: such, for instance, as sal ammoniac, the compound obtained by neutralising hydrochloric acid with ammonia; ammoniac nitrate, the salt obtained by neutralising nitric acid with ammonia; and ammoniac sulphate, the salt obtained by neutralising oil of vitriol with ammonia. All these salts crystallise in the same form as the corresponding salts of potassium with the same acids, and in every case the quantity of hydrogen present in the salt formed from ammonia is sufficient to convert it into the body ammonium, which seems to act as a compound metal, much in the same way as cyanogen is found to act like a compound halogen. For instance:—

Fig. 70.

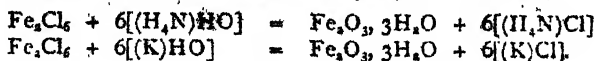


	Ammonia Salt		Ammonium Salt		Corresponding to Potassium Salt
Hydrochlorate	H_3N, HCl	=	$(H_4N)Cl$	=	$(K)Cl$
Nitrate	H_3N, HNO_3	=	$(H_4N)NO_3$	=	$(K)NO_3$
Sulphate	$(H_3N)_2, H_2SO_4$	=	$(H_4N)_2SO_4$	=	$(K)_2SO_4$

A solution of ammonia in water may, in fact, be regarded as ammonium hydrate, the analogous compound to potassium hydrate—



Upon this supposition, it is easy to explain the diverse position of a metallic salt and the separation of the oxide, on adding to it a solution of ammonia; as, for instance :—



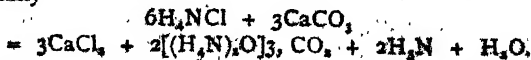
Exp. 220.—Dissolve a piece of sodium of the size of a pea, in about 2 cub. cm. of pure mercury, in a test-tube: the two metals unite suddenly with flame. When cold, pour the amalgam into a large watch-glass, and cover it with a saturated solution of sal ammoniac: the amalgam will gradually swell up and become pasty, and will often float when thrown into water.

This at one time was held to be an amalgam of ammonium $[(NH_4)_2Hg]$ dissolved in excess of mercury, but there is little doubt that it is simply mercury distended by hydrogen and ammonia gases, its bulk having been found to vary according to the pressure upon it—



It gives off hydrogen and ammonia on standing, and also when thrown into water.

One of the most remarkable of the salts of ammonium is the common smelling-salt, or sesquicarbonate, $2[(H_4N)_2O], 3CO_2$, which is obtained by heating a mixture of chalk with half its weight of powdered sal ammoniac, and subliming it gradually—



A large quantity of free ammonia escapes in the operation,

and the salt is always losing carbonate of ammonia, which causes its pungent smell; and a white powder, the bicarbonate, or hydric ammoniac carbonate, is left, $2[(H_4N)_2O], 3CO_2$ becoming $2H_4NHCO_3 + (H_4N)_2CO_3$.

A solution of sal ammoniac gives a yellow nearly insoluble double salt with platonic chloride ($2H_4NCl, PtCl_4$), which crystallises in cubes or octahedra, like the potassium salt. It is often used for ascertaining the quantity of an ammonium salt in solution. A still more delicate test is that known as Nessler's,* which gives a brown stain when the solution contains less than a millionth of its weight of a salt of ammonium.

GROUP II.—METALS OF THE ALKALINE EARTHS.

1. BARIUM. 2. STRONTIUM. 3. CALCIUM.

(48) 1. BARIUM: *Symb.* Ba; *Atomic Wt.* 137.

This metal is scarcely known in a separate state. When combined with oxygen, it forms *Baryta* (BaO), and a dioxide (BaO_2). *Baryta* (BaO) may be obtained by treating baric nitrate in a crucible till the salt, which decrepitates and melts, again becomes solid, and finally ceases to give off oxygen at a bright red heat. The baryta is left as a grey porous mass, which absorbs moisture and carbonic acid from the air. If mixed with half its weight of water it slakes, forming a hydrate, whilst great heat is given out. This hydrate is largely soluble in boiling water, and the solution deposits a crystalline hydrate of baryta as it cools. The liquid is strongly alkaline, and becomes milky by the action of carbonic acid.

The *dioxide* (BaO_2) may be formed by passing oxygen

* Nessler's test for ammonia is prepared thus: add to a solution of mercuric chloride a solution of potassic iodide, till the red precipitate first formed is nearly all dissolved. Then add a large excess of caustic potash; let the mixture stand in a stoppered bottle for three or four days, and decant when clear. It gives a brown precipitate when added to a solution containing a salt of ammonium. This consists of HgI_2, NI .

over anhydrous baryta at a low red heat; but if the heat be raised to full redness, the second atom of oxygen is given off again, and baryta is reproduced. If this oxide be dissolved at a low temperature in hydrochloric acid, baric chloride is formed, and the remarkable body H_2O_2 , hydrogen peroxide, is formed in the liquid—



The most abundant compounds of baryta are the sulphate and the carbonate.

The sulphate (BaSO_4) is a very heavy mineral, sp. gr. 4.6, the name baryta having been given to the earth in allusion to its weight, from *βαρύς*, 'heavy.' It is found crystallised in right rhombic prisms. It is insoluble in water and in solutions of the acids. It is easily obtained artificially by mixing a solution of a sulphate with one of baric chloride, or any soluble barium salt. This sulphate, although insoluble, furnishes a sulphide soluble in dilute acids if it be heated with carbon.

Exp. 221.—Grind about 10 grams of the sulphate to a very fine powder; mix it with an equal weight of flour, and make it into a paste with oil; place this mixture in a crucible, with a little charcoal; lute on the cover of the crucible with fireclay, and when the lid is dry raise the crucible gradually to an intense heat in a furnace, keeping it up for about an hour: then allow it to cool.

In this process the sulphate becomes reduced to sulphide, while carbonic oxide escapes—



Exp. 222.—Treat the residue, when cold, with a large quantity of boiling water. Everything should dissolve except the excess of carbon.

The sulphide thus obtained, if treated with hydrochloric acid, is dissolved, baric chloride is formed, and sulphuretted hydrogen escapes—



This chloride is one of the salts most often used for precipitating sulphuric acid from the sulphates. *Baric Carbonate* (BaCO_3) forms the mineral called *Witherite*, found occasionally in the lead veins in the north of England. It is insoluble in water; soluble with effervescence in dilute acids; and is easily obtained in the form of a white powder by mixing a solution of sodic carbonate with one of baric chloride or nitrate.

This carbonate, and all the soluble barium salts, are strongly poisonous, the best antidote being Epsom salts.

Tests for Barium Salts.—The best test for the barium salts in solution is the formation of a white precipitate, insoluble in nitric acid, on adding a solution of calcic sulphate. They communicate a green tinge to flame, and form, with a solution of sodic hyposulphite, a white sparingly soluble hyposulphite. This last test is useful as a means of distinguishing them from strontium salts, which, however, give a crimson colour to flame.

2. STRONTIUM: *Symb.* Sr; *Atomic Wt.* 87.5; *Sp. Gr.* 2.54.

This metal occurs chiefly combined as sulphate and carbonate in forms resembling the same compounds of barium, for which it was long mistaken; but its compounds are much less abundant. Its salts are not poisonous. The nitrate is used to give a red fire in the manufacture of fireworks. Strontic sulphate is rather more soluble than baric sulphate.

•(49) 3. CALCIUM: *Symb.* Ca; *Atomic Wt.* 40; *Sp. Gr.* 1.578.

This is a malleable metal of a very pale yellow colour. It is seldom prepared, but may be procured by decomposing its fused chloride by the voltaic battery. Calcium tarnishes quickly when exposed to the air. It forms but a single oxide (CaO), the very important substance known as lime, which is extremely abundant, both as carbonate and as

sulphate; the chalk and limestone rocks, as well as the different forms of marble, all consist of carbonate more or less pure. Compounds of calcium are also found in all fertile soils, and they occur in a large number of crystallised minerals, amongst which fluor spar, calcic fluoride, is one of the most important.

Calcic Oxide.—Lime (CaO): Atomic Wt. 56.—This is obtained by heating the pure carbonate for some time to bright redness, carbonic anhydride being expelled—



Exp. 223.—Place a few lumps of black marble in the open fire, or in an open crucible, with a hole at the bottom, and heat it strongly for an hour or two. When it is completely converted into quicklime, the lumps, when broken across, will be quite white.

Common lime is made by heating limestone for some days in a large egg-shaped or conical *kiln*, in which a fire is kindled at the bottom.

Freshly burnt lime is called *quicklime*. It is a white infusible substance, and if left exposed to the air it swells up gradually and falls to powder. If water be poured upon it great heat is given out, the earth swells up and combines with part of the water, and is said to become slaked. In this process a definite hydrate ($\text{CaO}, \text{H}_2\text{O}$) is formed: it is a light dry powder, from which the water may be driven out at a red heat.

Lime is sparingly soluble in water; the solution forms limewater, which is alkaline; and is often used as a test for the presence of carbonic acid, by which it is immediately rendered turbid.

Milk of lime is merely slaked lime diffused through water.

The great consumption of lime is in mortars and cements. Common mortar is made by mixing 1 part of lime into a thin paste with water, and adding 3 or 4 parts of sharp sand. It hardens slowly in the air, and gradually absorbs carbonic acid.

Limestones are rocks originally deposited in the form of mud from water, and vary in composition, sometimes being mixed with clay, sometimes with sand, or with other materials which alter their properties when burned. Common mortar is gradually dissolved away by the action of water, but when the limestone contains clay in moderate quantity it furnishes, after burning, a cement which hardens under water. Such lime is called *hydraulic lime*. It slakes much more slowly than pure lime.

Lime is moreover largely used as a manure, being especially useful in reclaiming peat or bog land, where it decomposes the excess of vegetable matter and renders the soil more open, while the lime becomes a carbonate.

Lime is used also in many chemical processes, as in converting the carbonate of potassium and sodium into caustic alkalis. It is used by the tanner to loosen the hair on hides by dissolving the outer surface of the skin, and it is employed to remove impurities from coal gas.

Calcic Chloride (CaCl_2) is made by dissolving limestone or chalk in diluted hydrochloric acid, and evaporating the solution. It may be obtained in deliquescent crystals with $6\text{H}_2\text{O}$; but when strongly heated it loses $4\text{H}_2\text{O}$, and leaves a porous mass still retaining $2\text{H}_2\text{O}$, which absorbs moisture greedily, and is often used for drying gases, which are allowed to pass slowly over it.

Calcic Sulphate, or *gypsum* ($\text{CaSO}_4, 2\text{H}_2\text{O}$), is an abundant and important mineral. When heated to about 500° it loses its water, and crumbles down to a white powder, which is extensively used for finishing the interior of houses, under the name of *plaster of Paris*. If the dry powder be made into a thin paste with water, the mixture becomes solid in a few minutes, owing to the recombination of the water with the sulphate, and expands slightly, eventually becoming as hard as the original gypsum. If the gypsum has been heated to redness it loses its porosity, and no longer 'sets' with water.

Exp. 224.—Select a medal suitable for the purpose; paste a shallow rim of paper round it, so as to make it like the lid of a pill-box, and anoint the surface of the medal very lightly with oil. Mix a little of the dry plaster with water till it becomes of the consistence of thin cream; apply it carefully with a hair pencil to every part of the surface, so as to exclude air bubbles; then pour a thicker mixture into the mould. Allow it to remain for an hour. The cast may then be removed: it will be a reversed copy of the medal.

Gypsum in certain cases forms a valuable manure. Calcic sulphate is a common impurity in spring waters.

Calcic Carbonate (CaCO_3 : Atomic Wt. 100).—Besides its occurrence in marble and in *Iceland spar*, which crystallises in rhombohedra, this carbonate is found in crystals of a different system, the prismatic, forming the mineral *aragonite*. It forms the different varieties of limestone, chalk, oolite, and calcareous marl, and is the principal constituent of corals, of the shells of fish, and of egg-shells, besides entering into the composition of the bones of animals in greater or less amount. It also forms a combination with magnesian carbonate, which is known as *dolomite* or *magnesian limestone*, which is very abundant in certain geological deposits. Many of these compact limestone rocks are highly prized for building. Portland stone is an oolite; that is, it is formed of little rounded grains, which resemble the hard roe of a fish in aspect.

Calcic carbonate is scarcely soluble in pure water, but it is freely dissolved by water containing carbonic acid, and is deposited again in crystals as the gas escapes. Enormous masses of the crystallised carbonate are thus formed in the lapse of ages. In the limestone hills of Derbyshire and other places, caverns occur where this process is always going on; water charged with carbonic acid and calcic carbonate makes its way through the roof of the cavern, where, as the carbonic acid gradually escapes, the carbonate is deposited in hanging columns, like icicles, termed *stalactites*, whilst the water falling upon the floor deposits a fresh portion of the

dissolved carbonate, which slowly grows upwards till the *stalagmite* so formed meets the stalactite depending from the roof, and thus a natural pillar of crystallised calcic carbonate is formed.

In volcanic districts, where the springs are often highly charged with carbonic acid, this deposition is often very rapid; the spring, as it escapes, deposits a porous material termed *tufa*, while upon sides of the stream a more compact substance, known as *travertine*, which is a sort of marble highly prized for building purposes, is formed.

Tests for Calcium Salts.—Solutions of these salts give no precipitate with ammonia, or with ammoniac sulphide, but they give a white one of calcic carbonate with sodic or potassic carbonate, as do also the salts of barium, and of strontium; from these they may be distinguished by means of a solution of *calcic sulphate*, with which calcium salts give no precipitate. *Ammonia oxalate* gives, in neutral or alkaline solutions of calcium salts, a white precipitate of calcic oxalate, soluble in nitric or hydrochloric acid, but not in acetic acid. They give a greenish yellow tinge to flame.

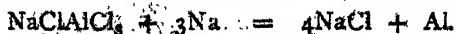
CHAPTER XII.

GROUP III.—METALS OF THE EARTHS.

(50) 1. ALUMINUM: *Symb.* Al; *Atomic Wt.* 27; *Sp. Gr.* 2.67.

This metal derives its name from alum, of which material it constitutes between 5 and 6 per cent. Its compounds are among the most abundant constituents of the rocks, including felspar, hornblende, and slate. Aluminum may be obtained from cryolite ($3\text{NaF}, \text{AlF}_3$) by fusing it with sodium; but the method usually practised consists in decomposing sodic aluminic chloride ($\text{NaCl}, \text{AlCl}_3$) by heating it with

sodium; an intense action occurs, and the aluminum is obtained in a melted state under the fused sodic chloride—



Aluminum is a white malleable metal, resembling zinc in colour and hardness. It may be rolled into foil, and drawn into wire. When struck, it gives a clear musical sound. It melts at a temperature below that needed for the fusion of silver. It preserves its brightness in the air, and is but slowly oxidized at a red heat. Nitric acid attacks it with difficulty, but it is rapidly dissolved by hydrochloric acid, and by solutions of the alkalis, hydrogen being given off. This metal, with about 90 per cent. of copper, forms a golden yellow alloy, called *aluminum bronze*, well fitted for castings.

Alumina (Al_2O_3).—There is only one oxide of this metal, the earth alumina, which, when crystallised, constitutes the Oriental ruby, the sapphire, and corundum. Emery is another form, of less purity. All these minerals are very hard; their colour is due to small quantities of the oxides of chromium, iron, or manganese. Alumina, combined with silica, forms the different varieties of clay, and is the basis of porcelain and earthenware. The soluble salts of alumina are of value to the calico printer. Hydrated alumina combines intimately with many vegetable colours, and forms with them pigments, called lakes.

Exp. 225.—Grind some madder root into a coarse powder, and pour a litre of boiling water upon three or four grams of it. Stir it up occasionally; then let it settle for three or four hours; pour off the red liquor. Mix it with a solution of 4 grams of alum, and add a solution of 4 grams of sodic carbonate. Let the solution rest in a tall glass jar; a red deposit or lake, consisting of the colouring matter combined with the alumina, will be produced.

If a pattern be stamped on calico with a solution of alum, and be then boiled with a solution of madder, the figures will be permanently dyed, while the colour may be easily washed out of the remainder of the cloth. In this case the alumina

in the alum fixes itself upon the cloth, and acts as a *mordant*, which 'bites in' the colour, or attaches it to itself, and thus renders the dye fast. Other oxides, such as those of iron, chromium, and tin, are used for the same purpose, but they change the colour of the dye stuff at the same time that they fix it upon the calico. All metallic oxides used for such a purpose are termed mordants by the dyer.

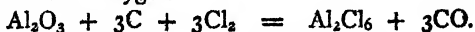
Alumina may be precipitated from its salts by a solution of potash, but an excess of potash redissolves the precipitate. Ammonia also precipitates the alumina as a bulky jelly-like hydrate, but does not redissolve it.

This hydrate is freely soluble in diluted acids, but the solution has the property of reddening litmus; so that, while the hydrate acts the part of a feeble acid towards potash and soda, which dissolve it, it also acts the part of a base towards acids, though it is but a weak base, compared with either potash or soda, or bases which contain, like them, 1 atom of oxygen with 2 atoms of a monad, or, like calcium, 1 atom of a dyad metal. Alumina resembles ferric and chromic oxides. It crystallises when united with acids in the same form as these oxides do when acted upon by the same acids, and consequently it is regarded as a sesquioxide.

The different basic oxides may be compared together in this manner:—

MONOXIDES		SESQUIOXIDES	
Monads	Dyads		
K ₂ O Potassic Oxide	CaO Calcic Oxide	Al ₂ O ₃ Aluminic Oxide	
Na ₂ O Sodid Oxide	FeO Ferrous Oxide	Fe ₂ O ₃ Ferric Oxide	
Ag ₂ O Argentic Oxide	CrO Chromous Oxide	Cr ₂ O ₃ Chromic Oxide	

Alumina forms a yellow chloride (Al₂Cl₆), which is volatile below a red heat. It is obtained by mixing alumina and powdered charcoal into a paste with oil, heating the mixture to redness, and sending a current of dry chlorine gas over it: the chlorine unites with aluminum, and the carbon with the oxygen—



The chloride is used in extracting the metal.

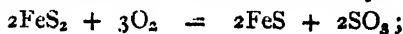
But the most important salt is the sulphate, which is obtained by treating clay for some days with sulphuric acid, at a heat nearly sufficient to make the acid boil. This sulphate (Al_2SO_4) is very soluble; but if mixed with a due proportion of potassic sulphate, it forms a salt, which crystallises in fine octahedra, and is well known as potassium alum ($\text{KAl}_2\text{SO}_4, 12\text{H}_2\text{O}$).

Alum is a double salt, which is made in vast quantities for the use of the calico printer. Ammonic sulphate is now largely employed instead of the potassic salt. It then produces ammonium alum ($\text{H}_4\text{N}, \text{Al}_2\text{SO}_4, 12\text{H}_2\text{O}$), which crystallises quite as readily and in exactly the same form as the potassium salt. The place of the aluminic sulphate may be supplied by ferric sulphate, chromic sulphate, and manganic sulphate. In each case a salt is formed, which is different in colour from true alum, but like it, and crystallises in octahedra, resembling those of alum; so that there are a number of alums known, some of which may be represented as follows:—

Ammonium Alum . . .	$(\text{H}_4\text{N})\text{Al}_2\text{SO}_4, 12\text{H}_2\text{O}$
Potassium Alum . . .	$\text{KAl}_2\text{SO}_4, 12\text{H}_2\text{O}$
Iron Alum . . .	$\text{KFe}_2\text{SO}_4, 12\text{H}_2\text{O}$
Manganese Alum . . .	$\text{KMn}_2\text{SO}_4, 12\text{H}_2\text{O}$
Chrome Alum . . .	$\text{KCr}_2\text{SO}_4, 12\text{H}_2\text{O}$

Alum has a sweetish, astringent taste. Its solution reddens litmus strongly. When heated it melts, first in its water of crystallisation, then it froths up, forms a tenacious paste, and at last becomes a white, bulky, porous, infusible mass, called *burnt alum*.

A good deal of alum is made by roasting alum schist (a kind of black bituminous clay, which contains a good deal of pyrites) for some weeks at a low temperature. The pyrites absorbs oxygen, and becomes gradually converted into ferrous sulphate, while the second atom of sulphur in the pyrites combines with oxygen, and the product unites with alumina, forming a mixture of aluminic and ferrous sulphates—



and on adding potassic chloride, alum crystallises out from the mixed sulphate and chloride of iron—



Silicates of Alumina—Clays.—Alumina forms a great number of silicates. All the varieties of clay consist of aluminic silicate, more or less mixed with other matters derived from the rocks which, as they have crumbled down, have furnished the clay. The best fire clay consists of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2, 2\text{H}_2\text{O}$. It is used in making bricks for lining furnaces, and for crucibles and glass pots, as well as for other purposes where resistance to a high temperature is required. But many kinds of clay contain lime, magnesia, or ferric oxide intermixed, and they greatly increase its fusibility, and diminish its plasticity, or fitness for kneading and moulding while in a moist state, and cause it to be more readily attacked by acids, while an excess of silica renders it less fusible. The more mixed varieties of clay constitute *marl* and *loam*. Pure clay forms, before it has been ignited and when kneaded with water, a tenacious plastic insoluble paste, which, when slowly dried and exposed to a high heat, shrinks very much, often splits, and becomes extremely hard, but does not melt in the furnace. Clay is not attacked readily by any acid except the hydrofluoric. Strong sulphuric acid, when strongly heated with it, gradually decomposes it.

When breathed upon, or slightly moistened, clay gives out a peculiar odour, and if applied in a dry state to the tongue or lips, it adheres to them strongly, and absorbs the saliva.

Felspar is a very abundant and important double silicate of aluminum and potassium ($\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$), often called *adularia*. When it contains sodium it is white, and is termed *albite*; and when it contains lithium, the mineral is known as *petalite*. Felspar is a very abundant constituent of the older rocks. Mixed with mica and quartz, it forms *granite* and *gneiss*. *Porphyry* is a compact felspar with crystals of felspar dispersed through it. *Basalt* is a dark-

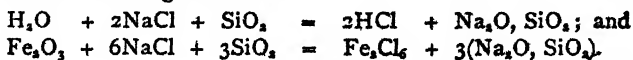
coloured volcanic rock, containing crystals of *augite* diffused through compact felspar. The porous *pumice* of volcanoes is chiefly felspar altered by high temperature; and *obsidian* is melted pumice. *Mica* is a more complex silicate of alumina, containing a little fluoride.

Earthenware and China.—The basis of these articles is silicate of alumina, but to diminish the tendency to crack during drying, which it has if used alone, the clay is mixed with ground flints, which, however, lessens its tenacity.* To make up for this defect, it is usual to add some fusible material which, at the temperature required for fusing, becomes softened, and greatly aids in binding the particles together. The clay thus mixed and tempered is moulded, while moist, upon the potter's wheel, after which the different articles are dried in a warm room, and are then fired at a comparatively moderate heat: they are thus obtained in a porous state, called *biscuit*. The patterns or designs are next applied, the colouring matter consisting usually of some metallic oxide ground up into a paste with turpentine or linseed oil. Blue is generally given by cobalt oxide, green by chromic oxide, brown by a mixture of the oxides of iron and manganese, black by uranium oxide, and so on. The ware, when painted, is much too porous for use; it is therefore glazed by dipping each article into water containing a fusible mixture, finely ground, in suspension. The porous mass quickly absorbs moisture, leaving a thin uniform layer of glaze upon the surface. The goods are then enclosed in fireclay vessels, and exposed to a furnace heat. The glaze melts, and leaves a smooth surface, so that the material is no longer porous and absorbent.

Stoneware is glazed differently. The pots are raised to a strong red heat in the furnace, and a quantity of damp salt is thrown in. The material is rapidly volatilised. The salt is decomposed by the silica and ferric oxide of the clay in

* In making crucibles and firebricks, old pots, finely powdered, are generally used instead of ground flints, but for the same purpose.

the presence of steam. Ferric chloride and hydrochloric acid pass off with the excess of salt employed, and form the dense brownish fumes which are seen escaping at intervals from the kilns on glazing days, while sodic silicate fuses on the surface of the ware, and makes it impervious to water, the actions being as follows :—



Tests for Aluminum Salts.—The solutions have a sweet, astringent taste. Potash gives a white precipitate, soluble in excess of the alkali. Ammonia, a white precipitate, insoluble in excess of the alkali. Carbonates of the alkalies, a white precipitate, insoluble in excess of the alkaline carbonate. Ammonic sulphide gives a white precipitate of hydrated alumina.

Exp. 226.—Heat a little alum on a platinum wire, bent into a small hook, in the outer flame of a Bunsen gas-burner. After the salt has been touched with a drop of a solution of cobalt nitrate, a pale blue compound of alumina and cobalt oxide will be formed. It is used as a blowpipe reaction for alumina.

2. *Glucinum* is the characteristic ingredient in the beryl and emerald. 3. *Yttrium* and (4) *Erbium* are both found only in a few rare minerals. 5. *Cerium* is met with rather more abundantly, accompanied by two other metals, (6) *Lanthanum* and (7) *Didymium*, in a mineral called *cerite*, but none of these are of sufficiently frequent occurrence to need further notice here.

GROUP IV.—MAGNESIUM METALS.

1. MAGNESIUM. 2. ZINC. 3. CADMIUM. 4. INDIUM.

(51) 1. MAGNESIUM: *Symbol*, Mg; *Atom. Wt.* 24.3; *Sp. Gr.* 1.74.

This metal is obtained by decomposing its chloride by means of sodium. It is purified by distilling it at a bright

red heat in a current of hydrogen. Magnesium is a malleable, ductile metal, of the colour of silver. It takes a high polish, which it preserves in a dry air ; but it becomes slowly oxidized in a moist atmosphere. At a moderate red heat it melts.

Exp. 227.—Heat a piece of magnesium wire in dry air or in the flame of a lamp : it takes fire, and becomes oxidized, producing white fumes of magnesia, giving out an intense white light.

This light is occasionally used for photographic purposes, or in lighting up the interior of buildings.

Magnesium is dissolved rapidly by diluted hydrochloric acid, giving off hydrogen ; and it is freely soluble in a solution of sal ammoniac. When heated in chlorine, or in the vapour of bromine, iodine, or sulphur, it burns brilliantly.

Magnesia (MgO).—This is the only known oxide of the metal. It occurs abundantly in combination as *dolomite*, or magnesian calcic carbonate ; as Epsom salts, or sulphate ; as chloride in sea water ; and as silicate in a variety of forms, both alone, as in talc and serpentine, and in combination with the silicates of alumina and other bases, as in *augite*, *hornblende*, and *asbestos* ; so that it is an important and frequent constituent of rocks. Magnesia is a bulky, white, tasteless, and nearly insoluble powder, obtained by strongly heating the carbonate or nitrate of the metal.

Exp. 228.—Place a little magnesia on moistened turmeric paper : it is sufficiently soluble to render the parts moistened, on which it rests, brown.

Exp. 229.—Place a small quantity of magnesian carbonate in a crucible : put on the cover, and heat the crucible in the fire for an hour. Take it out, and allow it to cool : caustic magnesia will be left. When moistened with water, it will not slake ; but if hydrochloric or nitric acid be poured upon the moistened earth, it will dissolve slowly, without effervescence.

Magnesian Chloride ($MgCl_2$) may be obtained by adding to a solution of one part of magnesia in hydrochloric acid three times its weight of sal ammoniac, evaporating to dryness, and heating the mixed salts to redness in a covered

crucible : the magnesian salt fuses, while the ammoniacal salt goes off in vapour. This chloride is deliquescent ; but if its solution be evaporated by itself, a good deal of hydrochloric escapes, and magnesia is left.

Magnesian Sulphate ($\text{MgSO}_4, 7\text{H}_2\text{O}$), familiarly known as Epsom Salts.—This is the most important soluble salt of the metal. It crystallises in four-sided solid prisms, which are very soluble, and have a bitter taste.

Tests for Magnesium Salts :—

Exp. 230.—Pour over 25 grams of Epsom salts 50 c. c. of boiling water : the salt dissolves, and part crystallises out as the solution cools. To a portion of the cold solution add a solution of sodic hydric carbonate : no precipitate occurs. Boil this mixture, and a white precipitate (the white magnesian carbonate), mixed with magnesian hydrate, is immediately separated.

Exp. 231.—Add to a solution of magnesian sulphate some ammoniac chloride ; then add a solution of hydric disodic phosphate. Stir the mixture : crystals of *ammoniac magnesian phosphate* are deposited in crystalline grains ($\text{MgH}_4\text{N}, \text{PO}_4, 6\text{H}_2\text{O}$), insoluble in water, containing ammonia in solution, but appreciably soluble in pure water. This is a very delicate test for magnesium salts, but it is readily dissolved by acids. Add a few drops of hydrochloric acid to the neutral solution : the precipitate disappears.

Exp. 232.—Collect a little of the crystalline precipitate in a filter ; dry it over a steam bath. Place a few decigrams of the dry salt in a small crucible, cover it, and weigh the whole ; then heat for ten minutes in a Bunsen gas-flame. Water and ammonia will be expelled. Allow the crucible to cool ; then weigh it a second time : it will be found to have lost weight considerably. The salt which is left is *magnesian pyrophosphate*—



Exp. 233.—Add to a solution of any magnesian salt, such as the sulphate, a solution of *potash* : a white precipitate of hydrated magnesia is formed. Excess of alkali does not redissolve it. *Limewater* produces a similar precipitate. *Ammoniac oxalate*, if mixed with an excess of solution of sal ammoniac, gives no precipitate with solutions of magnesium salts.

Exp. 234.—Place a little of the magnesium salt on a platinum wire moistened with a solution of cobalt nitrate. A pink residue will be obtained on heating the wire in the outer part of a Bunsen gas-flame.

(52) 2. ZINC or *Spelter*: *Symbol*, Zn; *Atom. Wt.* 65; *Sp. Gr.* 7.15; *Fusing Pt.* 412.

This well-known metal occurs chiefly in the form of sulphide, constituting *blende* (ZnS), or in that of carbonate, known to mineralogists as *calamine* (ZnCO_3). In order to extract the metal the sulphide is roasted, or heated moderately in a current of air: the sulphur burns off, and leaves the oxide. When calamine is roasted, water and carbonic anhydride are expelled, and zincic oxide is also left. The oxide, in either case, is next mixed with powdered coke, and heated. The carbon removes the oxygen as carbonic oxide, while the zinc, which is volatile at a full red heat, distils over, and may be condensed.

Zinc is a hard bluish-white metal, which, when a mass of it is broken across, shows a beautiful crystalline fracture. At ordinary temperatures it is rather brittle; but between 100° and 150° it may be rolled, and wrought with ease, though between 200° and 300° it again becomes brittle, and may be powdered. At 412° it melts, and it boils steadily at 1040° , and may be distilled at a bright red heat.

Exp. 235.—Heat a crucible to a bright red heat, and throw into it a few fragments of zinc. The metal will melt, and give off vapours which burn with great brilliancy, depositing clouds of zincic oxide.

Zinc soon tarnishes in a moist atmosphere; the thin film of oxide adheres closely to the metal, and protects it from further change. Dilute sulphuric and hydrochloric acids dissolve zinc rapidly, and give off hydrogen. Nitric acid also attacks it powerfully, but the acid itself is at the same time partly decomposed.

Zinc is often used as a substitute for lead in roofing; it is lighter and cheaper, but less durable. It is also used as the

active metal in the voltaic battery, and becomes dissolved in proportion as the electricity is liberated. Sheet iron is often coated with zinc, to render it less liable to rust; it then forms what is called *galvanised* iron. Brass is the most important of the alloys of zinc. It contains about two parts of copper to one of zinc, but the proportions of the two metals may be varied according to the purpose to which the alloy is to be applied. German silver is brass whitened by the addition of nickel.

Zinc Oxide (ZnO).—Zinc forms but one oxide, which is generally obtained in the form of a white flocculent powder by burning the metal in a current of air. When heated, this oxide becomes yellow, but on cooling it recovers its whiteness. It is easily soluble in the acids. If a solution of potash be cautiously added to a solution of a salt of zinc, such as the sulphate, a white gelatinous hydrated oxide is precipitated, but it is redissolved by an excess of potash: ammonia has a similar effect.

Zinc Sulphate ($\text{ZnSO}_4, 7\text{H}_2\text{O}$) is obtained in the ordinary process of preparing hydrogen by dissolving zinc in diluted sulphuric acid. It crystallises in white soluble prisms, resembling those of magnesian sulphate. It produces vomiting if swallowed in quantities, such as one or two grams.

The zinc salts are colourless; they have an astringent metallic taste. Sulphuretted hydrogen produces no precipitate in their acidulated solutions; but if mixed with a solution of ammoniac sulphide, a white gelatinous zinc sulphide is formed. A solution of sodic carbonate gives, with zinc salts, a white precipitate of hydrated basic zinc carbonate, not soluble in excess of the alkaline carbonate; but if ammoniac carbonate be used instead, the precipitate is redissolved by the addition of the ammoniac carbonate in excess. Zinc salts yield, with potassic ferrocyanide, a white precipitate.

Before the blowpipe, in the reducing flame, on charcoal, the metal is reduced and volatilised, burning into white

fumes of the oxide. *If placed on charcoal, and moistened with a solution of cobalt nitrate, they give, when heated in the oxidating flame, a green infusible residue.

3. CADMIUM : *Symb.* Cd ; *Atom. Wt.* 112.—This is a comparatively rare white, soft, easily fusible, volatilisable metal, usually found as sulphide, accompanying the ores of zinc in small quantity. Being more volatile than zinc, it comes over in the first portions which distil over during the reduction. It may be separated from zinc by dissolving these portions of the metal in sulphuric acid, and transmitting a stream of sulphuretted hydrogen gas through the solution ; a yellow cadmium sulphide is thus separated. This precipitate may be dissolved in hot hydrochloric acid, precipitated from the solution by the addition of ammoniac carbonate, and reducing the carbonate by heating it in an earthen retort with powdered charcoal ; the metal distils over at a red heat. It takes fire when heated strongly in air, and burns, forming a brown oxide. The addition of cadmium to the more fusible metals furnishes alloys of low melting point without destroying their toughness and malleability.

Cadmium furnishes a single oxide (CdO), which is brown when anhydrous, and white when hydrated. Ammonia dissolves it easily, but ammoniac carbonate does not dissolve it. Chloride and iodide of cadmium are used by the photographer. They crystallise easily.

4. *Indium* is a white soft metal, which has been found in small quantity occasionally associated with zinc. It was discovered by its property of furnishing, when heated in a colourless gas-flame, a light which is characterised by two strong lines in the indigo portion of the spectrum.

CHAPTER XIII.

GROUP V.—METALS ALLIED TO IRON.

1. COBALT. 2. NICKEL. 3. URANIUM. 4. IRON. 5. CHROMIUM.
6. MANGANESE.

(53) 1. COBALT: *Symb.* Co; *Atom. Wt.* 59; *Sp. Gr.* 8.95.

—This metal is never used in the arts in the metallic state, but it furnishes several compounds which are much valued for their beautiful colour. It generally occurs in combination with arsenicum, and is almost always found associated with nickel.

Metallic cobalt is obtained with difficulty in a pure state by a complicated process, for details of which some larger works on chemistry should be consulted. It is nearly as infusible as iron, is of a reddish grey colour, hard, ductile, and strongly attracted by a magnet.

Cobalt furnishes several oxides: two are well known—the protoxide (CoO), which, when treated with acids, yields the common salts of the metal, and the sesquioxide (Co_2O_3). These two oxides may be combined with each other in more than one proportion.

The protoxide is soluble in acids, and forms salts which, when anhydrous or in concentrated solutions, are of a beautiful blue colour; but they become pink in dilution. At a particular stage of dilution they become blue when heated, although when cold the solution is pink. This oxide is largely used for painting on porcelain, to which it imparts a rich blue colour.

- Smalt is a beautiful blue glass coloured with this oxide of cobalt. When finely powdered it forms the stone-blue used by laundresses to correct the yellow tinge in linen.

Cobalt Nitrate ($\text{Co}_2\text{NO}_3, 6\text{H}_2\text{O}$) is prepared by dissolving cobalt oxide in nitric acid. Its solution is sometimes employed as a test before the blowpipe. A fragment of the compound suspected to contain aluminum, magnesium, or zinc, is supported on charcoal, and touched with a minute

quantity of a solution of the nitrate: aluminous compounds give a blue residue if heated in the outer flame, those of magnesium a pink, and those of zinc a green residue.

Tests for Salts of Cobalt.—All the compounds of cobalt are easily distinguished before the blowpipe by the intense blue colour which they impart, even in minute quantity, to a bead of borax when fused with it on a loop of platinum wire. If the quantity of cobalt be large, the colour is so intense that it seems to be black.

Acid solutions containing cobalt are not precipitated by sulphuretted hydrogen, but ammoniac sulphide yields a black sulphide of cobalt. Solution of potash precipitates a rose-coloured hydrated oxide, insoluble in excess of the alkali. Ammonia and its carbonate also give a rose-coloured precipitate, soluble in excess of the alkali, forming a brownish solution, which absorbs oxygen from the air, and becomes red. It forms one of a large series of ammoniacal compounds which contain cobalt.

2. NICKEL: *Symb.* Ni; *Atom. Wt.* 59; *Sp. Gr.* 8·82.—This metal has a remarkable analogy with cobalt. It occurs associated with it in nature, has the same atomic weight, and is, like cobalt, powerfully attracted by the magnet. Its most abundant ore is *kupfernickel*, the arsenide (NiAs). The mode of its extraction is described in the book on 'Metallurgy.' Nickel is a brilliant silver-white, hard, ductile metal, nearly as infusible as iron. Its most important alloy is ~~German~~ man silver, which is a kind of brass whitened by the addition of about 20 per cent. of nickel.

There are two oxides of nickel, a protoxide (NiO) and a sesquioxide (Ni_2O_3); the first is the only one of importance. It is obtained by heating the nitrate or the carbonate to redness. It furnishes an olive-green powder. The hydrated oxide is of a delicate apple-green, and may be precipitated from its salts by the addition of a solution of potash, which does not redissolve it when added in excess. Acids dissolve

it and furnish pale green solutions. Ammonia precipitates the hydrated oxide from these solutions, but, if added in excess, redissolves the precipitate, and furnishes a blue liquid. Ammonic carbonate precipitates a green carbonate of nickel, soluble in excess of the alkaline carbonate.

3. URANIUM: *Symb.* U; *Atom. Wt.* 120.—This metal is scarcely known in its pure state. It occurs chiefly in the form of the black oxide (2UO , U_2O_3), which constitutes about 80 per cent. of the mineral *pitchblende*. The metal furnishes several oxides. The black oxide just mentioned is used as an intense black for painting on porcelain. The sesquioxide (U_2O_3) combines with the alkalies potash and ammonia, and forms a yellow compound. It is also soluble in acids, such as the nitric and acetic, and forms yellow salts, the solutions of which give a brown precipitate with potassic ferrocyanide, and a yellow precipitate with ammonia, not soluble in excess of the alkali. This oxide is used to communicate a peculiar opalescent yellow colour to glass, which exhibits the optical property of fluorescence in a remarkable degree.

(54) 4. IRON: *Symb.* Fe; *Atom. Wt.* 56; *Sp. Gr.* 7·84.—This, the most important of the metals, is also very abundant. It is found now and then in the metallic state, associated with nickel, cobalt, and some other elements, in those remarkable masses known as meteorites, which fall in an ignited state from the atmosphere from time to time—possibly the fragments of some formerly existing planet. For the supply of the vast demand for iron the ores chiefly wrought are magnetic ironstone, or loadstone (FeO , Fe_2O_3); specular iron ore (Fe_2O_3), or red hæmatite, which is a more abundant form of the same oxide; brown hæmatite ($2\text{Fe}_2\text{O}_3$, $3\text{H}_2\text{O}$), the hydrated sesquioxide; and spathic iron, or ferrous carbonate (FeCO_3). This last is the material which, when mingled with clay, furnishes the immense deposits of clay-ironstone which occur in what are called the

coal formations of Great Britain. Where this carbonate contains bituminous matter instead of clay, it constitutes the black-band ironstone of the coal fields on the Clyde.

In order to obtain iron from the ore, if in the form of clay-ironstone, it is broken up into masses about the size of the two fists, and then roasted in heaps to expel water and carbonic acid, by which process the ore is left in a porous state, highly favourable to its reduction in the blast furnace. These furnaces are usually about fifteen metres high, and in them a mixture of ore, coal, and limestone is subjected to intense heat, fresh supplies being added at the top as the materials sink down in the furnace. Powerful blowing machines supply air constantly near the bottom, and thus a steady and very powerful heat is maintained. The fuel burns, and is converted first into carbonic anhydride; and this becomes changed by the excess of carbon into carbonic oxide, which, meeting the descending charge, reduces its oxide to metallic iron. The reduced metal, mixed with the earthy matter of the ore, sinks down into the hotter region; here the lime, though infusible when heated alone, acts as a flux upon the clay of the ore: the two melt and become converted into an imperfect glass or *slag*, while the minutely divided iron combines with a portion of carbon of the fuel, and forms the comparatively fusible material known as cast iron. The slag and melted iron sink down to the bottom of the furnace; the iron, being much heavier, collects beneath the slag, and is run off at intervals of twelve or twenty-four hours into moulds formed in the sand of the floor, and, being afterwards separated from each other, form *pigs* of iron. The slag which collects on the surface of the iron before it is run off flows over continually at the opening left for the purpose on a higher level.

Cast iron, or pig iron, is brittle, and cannot be forged, though, if run into moulds, it takes impressions even of the finest lines. It never contains more than five per cent. of carbon; but it is not a pure carbide, for in the intense heat

the carbon of the fuel reduces not only the iron oxide, but also portions of silica, alumina, and lime, as well as phosphates and sulphates which are present. The cast iron, therefore, varies much in its quality, according as it contains more or less of carbon, silicon, sulphur, phosphorus, and other elements. When melted cast iron is allowed to cool slowly, part of the carbon crystallises out, and remains diffused through the mass in small flakes of graphite. This variety of the metal is known as *grey cast iron*. The same iron, if cooled rapidly, is crystalline in structure, and contains the carbon chemically combined, forming what is known as *white cast iron*.

In order to purify the pig iron, it is melted in a current of heated air, so as gradually to burn off the carbon, silicon, and other impurities, which are more combustible than the iron itself, the carbon escaping as carbonic oxide, the silicon as silica, and the phosphorus as phosphates. The silica, with the phosphates, unite with oxide of iron, and form a slag. The metal is thus rendered less and less fusible : it is collected by the workman into large balls, which are subjected while white hot to the blows of a powerful hammer, which squeeze out the melted slag ; and the metal, after being passed through grooved rollers, becomes converted into malleable iron, or wrought iron.

Iron, when combined with a smaller proportion of carbon than is contained in cast iron, furnishes *steel*, of which there are several varieties. The quantity of carbon in good steel varies between 0·7 and 1·7 per cent. That which possesses the greatest tenacity has been found to contain from 1·3 to 1·5 per cent. of carbon and about 0·1 of silicon. Fuller details of the mode of making cast iron, wrought iron, and steel, will be found in the text book on 'Metallurgy.'

Steel is more fusible than iron ; it is brittle, and when broken across shows a fine granular texture ; but its most characteristic property is that of becoming almost as hard as diamond when heated to redness and then suddenly cooled

by plunging into water or oil. It is thus rendered extremely brittle and almost perfectly elastic. This extreme hardness and brittleness may be removed by the process of *tempering*, which consists in reheating the hardened steel moderately, and then allowing it to cool. The higher the temperature to which it is raised in the second heating, the softer is the steel.

Exp. 236.—Allow a drop of nitric acid to fall upon a slip of polished steel : a dark grey spot is produced, owing to the solution of the metal in the acid, while the carbon is left. If the acid be dropped upon a slip of iron a green stain is formed.

Bar iron generally contains about 0·2 per cent. of carbon. It is hard, takes a high polish, is tough and fibrous, with a peculiar bluish-grey colour. It has a spec. grav. of 7·7. It requires the most intense heat of a wind furnace to melt it. It passes through a soft intermediate condition between actual fusion and solidity. This property is of the highest practical importance ; and it is owing to this fact that the smith is enabled, after sprinkling the surface of two white bars with sand, to *weld* them together so completely that the junction is as tough as any other part. The sand acts as a flux to the layer of oxide which forms upon the surface of the hot metal. A slag is thus formed upon each bar. By the blow of the hammer the film of melted matter is forced out, and the two clean surfaces of the metal become united.

Iron is susceptible of magnetism to a greater degree than any other known substance. At a high temperature it burns readily, as is seen in the vivid sparks thrown off from it when being forged, and the brilliant combustion exhibited by a coil of watch-spring or of wire, when heated and introduced into oxygen gas (*Exp.* 14). In dry air polished iron remains unaltered ; but if exposed to a moist atmosphere, so that liquid water be deposited on the metal, it quickly becomes rusty, and when once a spot of rust is formed the action proceeds rapidly. Iron may, however, be kept for any

length of time unchanged in water quite free from air, as well as in linewater, or in water containing a little caustic alkali. If steam be passed over red-hot iron, minute crystals of the magnetic oxide are formed, and hydrogen is given off (Exp. 44, Fig. 13).

Chlorine, bromine, and iodine combine quickly with iron, and dissolve it easily at common temperatures, as may be easily seen by placing a few drops of bromine under water in a test-tube and allowing a small quantity of iron filings to fall into the bromine. The iron will disappear, with a strong evolution of heat. Diluted sulphuric and hydrochloric acid dissolve the metal with escape of hydrogen (Exp. 45 and p. 60). The metal is rapidly attacked by nitric acid, with abundant escape of nitric oxide. Iron may, however, be kept unaltered in nitric acid of sp. gr. 1.45, or upwards; but if the acid be diluted below 1.35, it dissolves the metal with violence.

Iron yields four definite oxides: 1. The protoxide (FeO), the base of the green or ferrous salts; 2. The sesquioxide, the base of the red or ferric salts; 3. The black or magnetic oxide (FeO , Fe_2O_3), a compound of the two preceding oxides, which, when treated with acids, yields a mixture of ferrous and ferric salts, but no distinct saline compounds referable to it in constitution; and 4. *Ferric Acid*, an unstable metallic acid, the anhydride of which is unknown, but which forms salts, of which potassic ferrate (K_2FeO_4) is the representative.

Ferrous Oxide (FeO) is scarcely known in a pure state; it absorbs oxygen so rapidly. It forms a white hydrate; and if obtained by adding an alkali, such as ammonia, to a solution of ferrous sulphate, the white precipitate becomes green, passing into bluish green, black, and finally ochre-coloured, by the formation of sesquioxide. Ferrous salts, such as the chloride or sulphate, are obtained by dissolving the metal or its sulphide in hydrochloric or sulphuric acid, and allowing the solution to crystallise out of contact with air. These

salts have a delicate bluish-green colour, and an astringent, inky taste. If exposed to the air while moist, they become grass green, and slowly absorb oxygen.

Ferric Oxide (Fe_2O_3) is an abundant ore of iron. When anhydrous and crystallised, it forms specular iron ore. When in masses it furnishes hæmatite. Brown hæmatite anhydrate ($2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}$) is another abundant and valuable ore. In this form it is readily dissolved by acids. Jewellers' rouge is a finely-powdered red oxide, obtained by igniting the sulphate, as in the process for preparing the Nordhausen oil of vitriol.

When a ferric salt in solution, such as the chloride, is mixed with potash or ammonia, a milky reddish-brown hydrated ferric oxide is precipitated.

Iron combines with sulphur in several proportions. The *Protosulphide* (FeS) may be obtained as follows:—

Exp. 237.—Heat a bar of iron white hot in the fire, and bring it in contact with a roll of sulphur over a pail of cold water. The sulphur and iron immediately unite, and form drops of a reddish-brown colour, which run down into the water.

This sulphide is used in the laboratory for preparing sulphuretted hydrogen, which is disengaged without heat, by pouring upon it sulphuric acid diluted with 5 or 6 times its bulk of water.

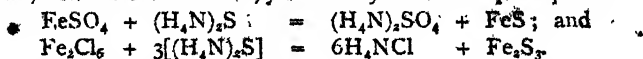
The *Disulphide* (FeS_2) is an abundant natural product. It forms the yellow brassy-looking mineral known as *iron pyrites*, often found crystallised in cubes.

Exp. 238.—Place a few fragments of pyrites in a small scaled tube, and heat it to dull redness in a lamp-flame; sulphur will gradually be sublimed.

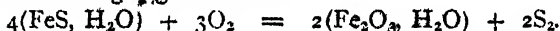
When heated in the air the sulphur burns off, and furnishes sulphurous anhydride, which is largely prepared from it for conversion into sulphuric acid. An impure oxide of iron is then left. Iron pyrites is not easily dissolved, except by nitric acid, or, still better, by a mixture of nitric with hydrochloric acid. *Mispickel* (FeAsS) is the name given to an arsenic sulphide of iron, which furnishes a good deal of the

arsenic of commerce. When heated in a current of air, it is converted into ferric oxide, while sulphurous and arsenious anhydrides are produced.

A solution of a ferrous salt, such as the sulphate, when mixed with ammoniac sulphide, yields a black hydrated ferrous sulphide, and in a similar way a solution of a ferric salt, such as the chloride, yields a hydrated sesquisulphide—



Both these sulphides, when exposed to the air, become converted into hydrated oxide, while the sulphur is separated without undergoing oxidation—



Ferrous Chloride, ($\text{FeCl}_2, 4\text{H}_2\text{O}$) may be obtained by dissolving the metal in hydrochloric acid, and evaporating the solution till it crystallises. *Ferric Chloride*, formerly known as sesquichloride (Fe_2Cl_6), may be obtained sublimed in anhydrous brown scales by heating iron wire to redness in a current of dry chlorine gas; it is very deliquescent. A solution of ferric chloride may also be obtained by passing a current of chlorine gas through a solution of ferrous chloride as long as the gas is absorbed, or it may be procured by dissolving hydrated ferric oxide in hydrochloric acid.

Ferrous Carbonate (FeCO_3) is found native in immense quantities. When crystallised, it is known as spathic iron ore; when mixed with clay, it forms the clay-ironstone; and when with bituminous matter, furnishes the blackband ironstone. Ferrous carbonate is also the salt which is found in chalybeate springs, in which it is held in solution by free carbonic acid. Mere exposure to air then causes its separation: the acid escapes, oxygen is absorbed, and hydrated ferric oxide, mixed with a small quantity of organic matter, subsides, forming the ochry deposits so common around ferruginous springs.

Tests for Iron.—The salts of this metal have an inky and astringent taste. The *ferrous* salts are known by the deep

blue precipitate which they give with the red prussiate (potassic ferricyanide) in solution. If one of the ferrous salts be heated with nitric acid, it is converted into a solution of ferric salt, while one of the lower oxides of nitrogen escapes. Ferric salts in solution are known by the rusty-brown precipitate of hydrated ferric oxide which they give with ammonia, by the blood-red solution produced by potassic sulphocyanide when added to an acid or neutral solution, by the bright Prussian blue precipitate occasioned by a solution of yellow potassic ferrocyanide, and by the bluish-black inky precipitate produced by tincture of galls in neutral solutions. This last is the colouring matter in ordinary writing-ink. Potassic ferricyanide gives no precipitate in ferric solutions, and thus may be used to distinguish them from those of ferrous salts.

Exp. 239.—Add to a solution of a ferric salt, mixed with a little solution of a salt of cobalt, a weak solution of ammonia, drop by drop, stirring the liquid between each addition, until the precipitate just begins no longer to be dissolved. The solution will become of a deeper red or yellow tinge. Dilute the liquid freely with water, and then boil it; an insoluble basic salt of iron will be formed, and every trace of iron may thus be precipitated, whilst the cobalt will remain dissolved, and may be found by adding a little more of ammonia.

(55) 5. CHROMIUM (*Symb.* Cr; *At. Wt.* 52.5) is never used as a metal, or even as an alloy, but is highly prized for the numerous brilliant-coloured compounds which it forms. The name chromium is derived from *χρῶμα*, colour. It is a rather rare element, and is most usually found in the chrome ironstone ($\text{FeO}, \text{Cr}_2\text{O}_3$).

The metal is very hard and infusible. It is sometimes obtained by heating chromic chloride with sodium. Chromium forms four well-known oxides: chromous oxide (CrO), which is unimportant; *chromic oxide* (Cr_2O_3), the basis of the common green or violet salts of the metal; it is prized as a green pigment for colouring porcelain; these two oxides corre-

spond to ferrous and ferric oxide in composition); a brown oxide ($\text{CrO}_2, \text{Cr}_2\text{O}_3$), corresponding with the magnetic oxide of iron, but which is unimportant; and a stable metallic anhydride (CrO_3), which, when dissolved in water, furnishes an important acid, from which the class of chromates is obtained.

The chromates are prepared on a large scale by heating chrome ironstone to redness, quenching in cold water to render it friable, then reducing it to an extremely fine powder, and heating to bright redness in a current of air, with a mixture of chalk and potassic carbonate. The mixture absorbs oxygen, and becomes yellow. When cold, it is treated with water, which dissolves out the chromates. Potassic carbonate is added as long as it occasions any precipitate of chalk from the solution of calcic chromate. The yellow solution is drawn off, mixed with nitric acid, and on evaporation potassic dichromate crystallises out in large red anhydrous prisms ($\text{K}_2\text{CrO}_4, \text{CrO}_3$), whilst nitric acid remains in solution.

This dichromate is the common commercial salt. It is a salt of exceptional composition, being a compound of the chromic anhydride with the mineral potassium salt. If formed in the regular way it would be composed as follows.



but such a salt is not known. The dichromate is soluble in about ten parts of cold water. If 4 measures of the cold saturated solution of this salt be mixed with 5 of oil of vitriol, and the liquid be allowed to cool, chromic anhydride crystallises in crimson needles, which may be drained and dried upon a brick.

Besides the dichromate, there is a normal chromate of potassium (K_2CrO_4), which is yellow, and does not crystallise easily; and there are also potassic salts known which contain two and three atoms of chromic anhydride combined with one atom of the potassic salt.

Baric chromate is a canary-yellow insoluble powder.

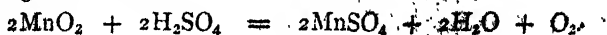
Chrome Yellow is the normal lead chromate (PbCrO_4). It falls as a bright yellow insoluble powder when a solution of lead acetate or lead nitrate is mixed with one of potassic chromate or dichromate. Argentic chromate (Ag_2CrO_4) is of a dark red colour, and is insoluble. Mercurous chromate ($3\text{Hg}_2\text{CrO}_4, \text{Hg}_2\text{O}$), obtained by adding mercurous nitrate to a solution of a chromate, is orange coloured and nearly insoluble. The chromates of cadmium and bismuth are yellow.

If a soluble chromate, such as potassic chromate, be mixed with hydrochloric acid, chromic acid and a chloride of the metal are formed in the solution; and if a little alcohol or sugar be added, and the liquid be boiled, it becomes green, owing to the reduction of the chromic acid to chromic oxide, which becomes dissolved in the excess of hydrochloric acid. If to this green solution ammonia be added in excess, a pale green hydrated chromic oxide is precipitated. This may serve as a distinctive test for the chromates.

6. MANGANESE: *Symbol*, Mn, *Atomic Weight*, 55.—This is an element which is widely diffused, and enters into the formation of many minerals in small quantity, but its only important and valuable ore is the black oxide, found either in masses or in radiated groups of crystals.

The metal is not used alone, but it is often present in small quantity in cast iron. It is difficult to obtain manganese in a state of purity, as it possesses a powerful attraction for carbon, so that, if reduced, as it may be without much difficulty, by making the carbonate into a paste with oil, and heating it in a covered crucible lined with charcoal, and keeping it for an hour at the highest heat of a forge, the button of metal is always combined with carbon. It also, like iron, combines with silicon. Manganese is a hard, brittle, greyish-white metal, and is feebly magnetic. It is remarkable for the number of oxides which it forms. Manganous oxide (MnO) is the basis of the common salts of the

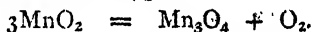
metal; the sesquioxide (Mn_2O_3) is unimportant, and does not furnish stable salts. The red oxide (Mn_2O_3) may be regarded as the compound of the two preceding ones; it corresponds to the magnetic oxide of iron, and furnishes no corresponding salts. The black oxide or dioxide (MnO_2) is the most important native compound of the metal; when treated with acids, it gives off half its oxygen, and furnishes manganous salts—



With hydrochloric acid it yields chlorine and manganous chloride—



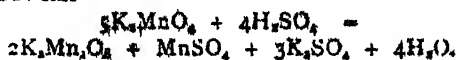
and if heated alone, it yields oxygen and the red oxide, giving off one-third of its oxygen—



When found native, it is called grey manganese ore, or *pyrolusite*. Another variety, in warty masses, is *psilomelane*, and a hydrated form is called *wad*. It is often found mixed with earthy carbonates, and other impurities. Besides the above-mentioned oxides, manganese forms two others, which are not known in a separate state (MnO , and Mn_2O_7), which, when dissolved in water, furnish manganic and permanganic acids. The manganates are of a green colour. *Sodic Manganate* (Na_2MnO_4) is prepared on a large scale by heating a mixture of caustic soda and finely powdered manganese to dull redness for several hours in shallow vessels. Its solution forms Condyl's green disinfecting liquid. This green substance furnishes an excellent method of distinguishing before the blow-pipe, for if the substance be heated on platinum foil, with a little sodic carbonate, it gives a green colour to the melted mass if a trace of manganese be present.

Solutions of the manganates part very readily with oxygen; they must not even be filtered through paper. A small quantity of a free acid changes their solution from green to

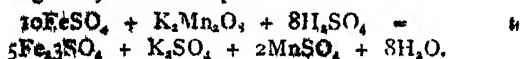
red, owing to the formation of a permanganate and of a manganous salt—



Potassic Permanganate ($\text{K}_2\text{Mn}_2\text{O}_8$) may be obtained on a small scale by mixing 40 grams of finely-powdered manganese dioxide with 35 grams of potassic chlorate, and adding a solution of 50 grams of caustic potash to the mixture, evaporating to dryness, and heating the powdered residue to dull redness in a clay crucible. When cold, the mass is treated with water, and decanted from the insoluble residue; a splendid purple liquid is obtained, which on evaporation yields needles of the permanganate. A solution of this salt is very readily deoxidised and deprived of colour. It furnishes a valuable test liquid in many cases of volumetric analysis.

Exp. 240.—Dissolve two or three decigrams of iron wire in diluted sulphuric acid; then add water till the liquid measures about half a litre. Add gradually a solution of the permanganate, and stir the mixture: the colour will disappear until the whole of the iron has passed from the state of ferrous into that of ferric salt. When this point is reached, the pink colour of the permanganate will remain unchanged.

The change may be thus represented —



Tests for Manganese.—Manganous chloride is formed in large quantities in the ordinary mode of preparing chlorine. The manganous salts are of a delicate pink colour, and give nearly colourless solutions. They give with ammonia a white hydrated manganous oxide, soluble in excess of the alkali; but the solution quickly absorbs oxygen, and deposits a brown hydrated peroxide. Ammoniac sulphide precipitates a flesh-coloured hydrated manganous sulphide. Solution of potassic carbonate precipitates a white manganous carbonate. Before the blowpipe they give, with sodic car-

bonate on platinum foil, the characteristic green-coloured manganate; and they give in the oxidising flame, with a bead of borax, a violet colour, which disappears in the reducing flame.

CHAPTER XIV.

GROUP VI.—TIN AND ALLIED METALS.

1. TIN. 2. TITANIUM. 3. ZIRCONIUM. 4. THORIUM.

(56) TIN: *Symb* Sn. *Atom.* 112. 118; *Sp. Gr.* 7.29; *Fusing Pt.* 228°.

This familiar metal was known in the early ages of the world. It is not found in many places, Cornwall and Malacca supplying the greatest portion. The only ore of tin of importance is its dioxide, or *tinstone*, which is often found crystallised. After the ore has been crushed, and roasted to get rid of arsenicum and sulphur, and washed to remove the oxides of iron and copper which are formed from the pyrites by which it is accompanied, the metal is reduced by heating the residue with powdered anthracite or charcoal.

Tin is a white metal, with a tinge of yellow, and a high lustre, which it preserves unchanged in the atmosphere. It is rather soft, and very malleable, so that it is easily reduced into sheets of *tin foil*, but it is not sufficiently tough to be drawn readily into wire. It melts easily (about 228° C.), but is not volatilised in the furnace. It has a considerable tendency to crystallise.

Exp. 241.—Warm a sheet of tinplate over a lamp, and then pour over its surface a mixture of nitric and hydrochloric acids diluted with 8 or 10 parts of water. In a few minutes crystalline flakes will appear. They may be rendered permanent by washing off the acid, drying the plate, and varnishing it.

If heated to bright redness in the air, tin burns with a white light, and furnishes the dioxide.

Hydrochloric acid, if heated with tin, dissolves it slowly, with escape of hydrogen, forming stannous chloride (SnCl_2), one of its most important salts. Nitric acid of sp. gr. 1.3 oxidises it violently, and forms a white hydrated oxide, known as metastannic acid, but does not form a nitrate. Tin also combines easily with sulphur, phosphorus, chlorine, and bromine, when heated with them.

Tin forms several important alloys. Tinplate consists of sheet iron which has been cleansed from oxide, and coated with tin by plunging it into a bath of the melted metal. Pewter is an alloy of 4 parts of tin and 1 of lead. Plumbers' solder is a fusible alloy of equal parts of tin and lead. Britannia metal is composed of equal parts of brass, tin, antimony, and bismuth; it is much used for making common spoons and teapots.

Copper and tin form several valuable alloys. *Brass* is a combination of copper, tin, and zinc, with 5 or 6 per cent. of tin and 3 or 4 of zinc. *Gun metal* contains 9 or 10 per cent. of tin, *bell metal* about 22 per cent., and *speculum metal* about 33 per cent. Tinfoil, when amalgamated with mercury, forms the silvering applied to the backs of mirrors.

Tin forms two oxides, stannous oxide (SnO) and stannic oxide (SnO_2). The *Stannous Oxide* may be obtained as a white hydrate by adding a solution of sodic carbonate to one of stannous chloride: carbonic anhydride escapes, and the hydrated tin oxide is precipitated. It is soluble in an excess of caustic potash, but not in excess of ammonia. This oxide, when moist, absorbs oxygen from the air. It is soluble in acids, and furnishes the stannous salts, of which, however, stannous chloride is the only one of considerable importance.

Stannic oxide, the dioxide (SnO_2), constitutes the ore of tin. It is in this form very hard, and is insoluble in acids; but when powdered and fused with potash or soda, it combines with the alkali, and becomes soluble in water. When combined with water, this oxide furnishes a feeble metallic

acid, which is itself readily soluble in diluted acids, though it furnishes salts called stannates.

Sodic Stannate ($\text{Na}_2\text{SnO}_3, 3\text{H}_2\text{O}$) may be prepared by fusion, as above described; it is used, under the name of tin-prepare liquor, by the calico printer as a mordant for fixing certain colours.

Another hydrate of this oxide, possessed of entirely different properties, is obtained by treating metallic tin with nitric acid. It is called *Metastannic Acid* ($\text{H}_2\text{Sn}_3\text{O}_{11}, 4\text{H}_2\text{O}$), and is quite insoluble in other acids. It also forms unstable salts, such as potassic metastannate ($\text{K}_2\text{Sn}_3\text{O}_{11}, 4\text{H}_2\text{O}$). When metastannic acid is heated to redness, it loses all its water, and furnishes a pale buff-coloured substance, sometimes called *putty powder*.

Tin forms two well-marked sulphides. *Stannous Sulphide* (SnS) is thrown down as a chocolate-brown hydrate when a stream of sulphuretted hydrogen is passed through a solution of stannous chloride or other stannous salt. It is dissolved by a solution of ammoniac disulphide.

Stannic Sulphide (SnS_2) may be obtained as a hydrate, of a dingy yellow colour, by transmitting sulphuretted hydrogen through a solution of a stannic salt, such as stannic chloride; and it is readily dissolved by ammoniac sulphide, with which it forms a soluble double sulphide. A similar double salt may be obtained in crystals ($2\text{Na}_2\text{S}, \text{SnS}_2, 12\text{H}_2\text{O}$), if sodic sulphide be used as the solvent.

Stannic sulphide may be obtained in beautiful yellow flakes, forming *mosaic gold*, by heating an amalgam of tin with sulphur and sal ammoniac; but the operation requires care.

Stannous Chloride ($\text{SnCl}_2, 2\text{H}_2\text{O}$), the *tin salts* of the dyer, may be obtained crystallised in needles by dissolving tin in strong hydrochloric acid, and evaporating the liquid. It has a strong attraction both for chlorine and for oxygen. It therefore acts as a powerful reducing agent.

Exp. 242.—Add to a solution of corrosive sublimate a drop

or two of a solution of stannous chloride: a white precipitate of calomel is formed—



Now add the tin salt in excess: the precipitate becomes dark grey. It consists of metallic mercury, which may be collected into globules—



The calomel loses the whole of its chlorine.

Stannous chloride is used by the dyer for deoxidising indigo and the peroxides of iron and manganese.

Stannic Chloride (SnCl_4) is a colourless liquid, which emits dense fumes in the air, boiling at 115°C ., and combining with water greedily, to form a crystalline hydrate, which is soluble in a further quantity, but is decomposed by copious dilution, stannic acid being precipitated, while hydrochloric acid is set free. The precipitate is readily redissolved by an excess of acid. Stannic acid is easily obtained from this chloride by the cautious addition of sodic carbonate to the solution. This chloride is prepared without difficulty by distilling 1 part of tin filings with 4 parts of corrosive sublimate, $2\text{HgCl}_2 + \text{Sn}$ yielding $\text{SnCl}_4 + 2\text{Hg}$. Exposure to the fumes must be carefully avoided.

Tests for Tin.—In addition to reactions mentioned when speaking of stannous oxide and stannous chloride, the stannous salts are characterised by giving in a dilute solution, if mixed with a solution of amic chloride, a beautiful purple precipitate, 'the purple of Cassius'; but if the tin salt be in excess, a brown precipitate of reduced gold is formed. Before the blowpipe on charcoal, tin salts yield a malleable white bead of the metal.

Tin belongs to the group of tetrad elements, and presents a certain analogy with silicon in its mode of combination. It is still more closely allied to the rare bodies *titanium*, *zirconium*, and *thorium*, which, however, are not of sufficient practical importance to need notice here.

Molybdenum is found as a sulphide resembling blacklead

in appearance; and *tungsten* is a heavy, black, hard mineral, called *wolfram*. It is unnecessary to describe further the compounds of molybdenum and tungsten, or those of *niobium*, *tantalum*, and *vanadium*: for particulars respecting them the reader is referred to systematic treatises on Chemistry.

CHAPTER XV.

I ARSENICUM. 2. ANTIMONY. 3. BISMUTH.

(57) I ARSENICUM: *Symb.* As; *Atom.* 75; *Sp. gr.* of solid, 5.95, of vapour, 10.6; *Atom. Vol.* $\frac{1}{2}$; *Mol. Vol.* $\frac{1}{2}$; *Rel. Wt.* 150.

This highly poisonous substance exhibits characters intermediate between those of the non-metals and the metals. It conducts electricity in a moderate degree, and possesses high metallic brilliancy; but it much resembles phosphorus in general properties, including its anomalous vapour density. It is usually found in the form of an alloy with some other metal, especially with iron, cobalt, nickel, or copper. Now and then it is found native, and occasionally in the form of a metallic arseniate.

In the preparation of the metal native arsenide of iron or of cobalt is *roasted*, or heated in a current of air. The arsenicum becomes oxidized, and forms arsenious anhydride (As_2O_3), or white arsenic, which is volatilised below a red heat, and becomes condensed again as it cools in the flues, or in chambers constructed to receive it.

In order to obtain the metal, this white oxide is powdered, mixed with charcoal, and heated in a crucible, upon the top of which a second inverted crucible is luted; and this is screened from the fire by means of a perforated iron plate. Carbonic oxide is formed, and escapes, while the metal, which is also volatile below redness, sublimes, and is condensed in the cool inverted crucible. The metal, however,

is not often wanted. It is very poisonous, both alone and when in combination, and requires great care in experimenting with it.

Exp. 243.—Take a fragment of white arsenic, the size of a pin's head; crush it to a fine powder, and mix it with 3 or 4 times its bulk of powdered charcoal. Introduce the mixture into a glass quill tube, sealed at one end and 8 or 10 cm. long. Warm the mixture gently, so as to drive off the moisture which the charcoal usually contains. This, when condensed, may be removed from the tube by introducing a small roll of filtering-paper. Then heat the end of the tube containing the mixture to redness. A dark steel-grey metallic mirror-like sublimate of reduced arsenicum will be condensed on the cool sides of the tube, and a distinct garlic-like odour will generally be perceived.

Arsenicum is very brittle; it has a brilliant dark steel-grey lustre, and volatilises before it melts, at a temperature of about 180°C . It gives off a colourless vapour, with an oppressive garlic-like smell. If heated in air, it combines with oxygen, and becomes converted into arsenious anhydride, which condenses upon somewhat warm surfaces in transparent brilliant octahedra.

Exp. 244.—Cut off with a triangular file the portion of the tube containing the mirror of arsenicum obtained in the last experiment. Crush the glass and put the fragments into another sealed quill tube, and heat the broken portions gently: the metal will be sublimed, but will combine with the oxygen of the air in the tube, on the cool sides of which, by the aid of a pocket lens, octahedra of arsenious anhydride may be seen condensed.

Arsenicum takes fire if thrown in powder into chlorine gas, and it combines readily with bromine, iodine, and sulphur, if gently heated with them. Nitric acid oxidises the metal rapidly. Hydrochloric acid has but little action, unless a little nitric acid or nitre be added.

Arsenicum is alloyed in small quantity with lead, to facilitate its taking a globular form in the manufacture of shot. It is also used in combination with copper and oxygen in the preparation of certain green pigments; and orpiment,

which is a yellow largely employed, is one of the sulphides of the metal.

Arsenicum forms two compounds with oxygen (As_2O_3 and As_2O_5), both of which, when combined with water, form acids.

Arsenious anhydride, or *White Arsenic* (As_2O_3), is obtained usually as an opaque milk-white mass, often containing small portions or layers of the transparent crystalline form of the compound. It is but sparingly soluble in cold water, but more so in boiling water, and still more readily in hydrochloric acid. Alkaline solutions dissolve it easily, and furnish a solution of arsenite of the metal, which does not crystallise. When heated to about 190° the anhydride softens, and sublimes before fusing. Its vapour is colourless, extremely dense (of sp. gr. 13.8), and it contains 1 volume of the vapour of the metal and 3 of oxygen condensed into 1 volume, being double the density that its composition would have led us to expect.

Exp. 245.—Boil 1 gram of arsenious anhydride with 3 of potassic carbonate in 100 c. c. of water till it is dissolved, and add it to a solution of 3 grams of cupric sulphate in 100 c. c. of water: a beautiful green precipitate of *Scheele's Green* (CuHAsO_3) will be obtained.

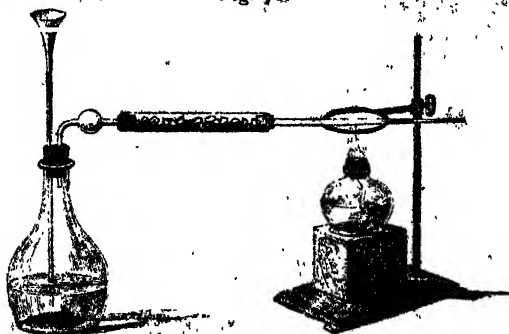
Exp. 246.—Add a few drops of a solution of arsenious anhydride to 200 or 300 c. c. of water, and then 3 or 4 c. c. of hydrochloric acid; place in the liquid two or three slips of bright copper foil, and boil the whole for a few minutes: the copper foil will become coated with a steel-grey film. Part of the copper becomes dissolved, and displaces the arsenicum, which is thrown down on the undissolved portion. Pour off the water, dry the copper on blotting-paper, and heat the foil in a gull tube, sealed at one end. The arsenicum will be oxidized and will sublime, condensing in minute octahedra on the cold sides of the tube.

This is *Reinsell's test* for arsenic. *Marsh's test* may be made as follows:—

Exp. 247.—Into a wide-mouthed flask of the capacity of 150

or 200 c. c., fit a cork provided with a tube funnel passing nearly to the bottom, and with a second bent tube, which may have a bulb blown upon it, as shown in Fig. 71. This is to be connected by means of a cork with a wider tube loosely filled with calcic chloride. To the end of this drying-tube attach a piece of quill tube, free from lead, drawn out into a capillary end. In the flask place a few fragments of pure zinc, or, better still, of magnesium foil. Then pour on some water, and add a sufficient quantity of pure sulphuric acid to cause a steady

Fig. 71.



formation of hydrogen. When all the air has had time to be displaced, apply the flame of a lamp to the shoulder or beginning of the narrowed part of the tube. Add through the funnel two or three drops of a solution of arsenious acid. Immediate voltaic action will occur; the arsenious acid will be deprived of its oxygen, and part of the metal will at the instant combine with hydrogen, forming arseniuretted hydrogen. This gas will be separated into arsenicum and hydrogen as it passes through the heated tube, and the metal will be deposited as a steel-grey ring just beyond the spot at which the heat is applied.

Arsenic Anhydride (As_2O_3) may be obtained by boiling arsenious anhydride with nitric acid, and evaporating to dryness. It is very soluble in water, and forms a powerful tribasic acid, which furnishes salts; these present a very close resemblance to the tribasic phosphates. When united with the same metal, the arseniate and phosphate crystallise in

exactly the same form, and with the same number of molecules of water of crystallisation.

The hydric disodic arseniate ($\text{Na}_2\text{HAsO}_4, 12\text{H}_2\text{O}$) is made in large quantity for the calico printer and dyer. The potassic dihydric arseniate (KH_2AsO_4) crystallises in fine octahedra, which are easily obtained by throwing a mixture of equal parts of nitre and arsenious anhydride into a red-hot clay crucible. Allow the mass to cool, dissolving the residue in a small proportion of water, and setting it aside to crystallise.

Arsenicum and sulphur combine in several proportions: the red compound (As_2S_2), is called *realgar*; *orpiment* is As_2S_3 ; and there is another sulphide, As_2S_5 ; these two last correspond to arsenious and arsenic anhydride.

Orpiment is easily made by passing sulphuretted hydrogen through a dilute solution of arsenious acid in hydrochloric acid. Orpiment melts easily: it is soluble in ammonia, as well as in potash and soda, and in a solution of an alkaline sulphide.

Only one compound of chlorine and arsenicum, the trichloride (AsCl_3), is known. It is liquid and volatile. Corresponding compounds with bromine and iodine are solid.

Arseniuretted Hydrogen (AsH_3). (*Mol. and Atomic Wt.* 78; *Sp. Gr.* 2.695; *Relative Wt.* 39; *Mol. Vol.* 11.)—Arsenicum forms a remarkable gaseous compound with hydrogen, which is a deadly poison. It is neither acid nor alkaline, but it has a close analogy with phosphuretted hydrogen, and with ammonia. It is nearly insoluble in water, but is absorbed with decomposition by solutions of cupric sulphate, of corrosive sublimate, and of argentic nitrate. In the last case, metallic silver and arsenic acid are formed—



Its decomposition, when heated, is turned to account in Marsh's test for arsenic.

(58) ANTIMONY: *Symb.* Sb; *Atoms. Wt.* 122; *Sp. Gr.* 6.71; *Fusing Pt.* about 620°.

This metal is always extracted from the sesquisulphide, which is a bluish-white lustrous mineral, crystallised in four-sided prisms, striated across their length. This sulphide is brittle, and melts below a red heat, crystallising as it cools. The *crude antimony* of commerce is the sulphide freed by fusion from its earthy impurities. The metal is easily obtained in small quantities by mixing 4 parts of this sulphide with 2 of pearlash and $1\frac{1}{2}$ nitre, powdering and mixing them intimately, and throwing the powder in small portions at a time into a crucible kept at a bright red heat. The quantity of nitre used is not sufficient to oxidise both the sulphur and the metal; and as the sulphur is the more combustible element, it burns, while the metal melts, and collects beneath the melted slag of potassic sulphate.

Antimony is a brilliant bluish-white metal, crystallising in plates, and is so brittle that it may be easily powdered in a mortar.

It melts just above a red heat, and burns brilliantly in a current of air, giving off white fumes, composed chiefly of antimonious oxide. Powdered antimony takes fire when thrown cold into chlorine gas, and it combines energetically both with bromine and with iodine. Nitric acid and aqua regia oxidize it with violence; and if powdered, and boiled with sulphuric acid, it is converted into a sulphate. The metal, in fine powder, digested with a persulphide of one of the alkali metals, is dissolved.

Antimony is too brittle to be used alone, but it is useful for hardening other metals when alloyed with them. Type metal is an alloy of lead with about one-fourth of antimony, and often about the same quantity of tin is added.

The oxide, when ground up with linseed oil, furnishes a white pigment, inferior, however, to common white lead; and tataric emetic, a salt of tartaric acid with potassium and antimony $2[K(SbO)C_4H_4O_6]H_2O$, is a very active medicine.

Antimony forms three oxides : Sb_2O_3 , the sesquioxide, is a feeble base, which is freely soluble in hydrochloric and in tartaric acid ; Sb_2O_5 is a metallic anhydride ; it furnishes salts with bases called *antimoniates* ; and Sb_2O_4 is a compound of these two, which is formed by heating either of the other oxides in a current of air.

Antimony combines with hydrogen, and forms a colourless gas, much resembling arseniuretted hydrogen, but with no special odour. It may be obtained by dissolving an alloy of zinc and antimony in diluted sulphuric acid. When a solution of any antimonious salt is added to a mixture of zinc and sulphuric acid which is giving off hydrogen, the antimonial salt is decomposed, and antimoniuretted hydrogen comes off mixed with the free hydrogen. It is decomposed when passed through a red-hot tube, and a brilliant crust of metallic antimony is deposited. When the gas is burned in the air, white clouds of antimonious oxide are formed.

Antimony forms two sulphides (Sb_2S_3 and Sb_2S_5), which correspond to the two principal oxides. They are both soluble in the solutions of the sulphides of the alkali metals, and combine with them to form definite crystalline compounds, or *sulphur salts*.

The *sesquisulphide* (Sb_2S_3) is the ore of the metal, but it may also be obtained artificially in beautiful orange-coloured flocculi, by sending a current of sulphuretted hydrogen through a solution of tartar emetic, or other soluble antimonious salt. The formation of this compound furnishes one of the best tests for antimony. It is soluble with escape of sulphuretted hydrogen in hot hydrochloric acid.

The metal forms two chlorides (SbCl_3 and SbCl_5), which correspond to the oxides and sulphides. The *trichloride* (SbCl_3) is a fusible solid, which is a strong caustic. It is soluble in hydrochloric acid ; but, on dilution, unless the quantity of acid be very large, an insoluble oxychloride ($\text{SbCl}_3 \cdot \text{Sb}_2\text{O}_3$) falls as a white powder, readily soluble in tartaric acid. If antimony is heated with chlorine in excess,

it forms the pentachloride (SbCl_5), a fuming volatile liquid, which is decomposed by a large quantity of water.

The compounds of antimony are powerful irritant poisons. Antimony is more likely to be mistaken for arsenic than for any other metal. The crust which is formed by decomposing antimoniuiretted hydrogen in Marsh's apparatus does not yield octahedra, when sublimed in a tube with air, but prisms. The metal is also easily soluble in yellow ammonium sulphide, which is nearly without effect upon arsenical crusts.

(59) BISMUTH: *Symb.* Bi: *Atom. Wt.* 210; *Sp. Gr.* 9.8; *Fusing Pt.* 264°.

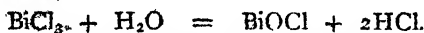
This metal is found but rarely, and is generally met with in the native state in quartz rock, from which it is commonly separated by simple fusion. It is hard, brittle, and of a reddish-white colour. It may be crystallised more readily than any other metal; and it furnishes large hollow cubes by fusion and slow cooling, pouring off the inner part before the whole has become solid. Bismuth does not become tarnished by exposure to the air at ordinary temperatures, but it is rapidly oxidized in a current of air at a red heat. If thrown in powder into chlorine gas, it takes fire; and it combines easily with bromine, iodine, and sulphur. Nitric acid is its best solvent. The nitrate crystallises in flat, transparent, colourless prisms.

This metal is not used alone, but it enters into a remarkably fusible alloy, which may be prepared by melting together 2 parts of bismuth, 1 of lead, and 1 of tin. This mixture melts at a little below 100° C.; and as it expands in setting, it is valuable to the die-sinker, as it enables him to take sharp and faithful impressions of his work from time to time during its progress. Bismuth forms two principal oxides: Bi_2O_3 , which is basic, and is easily obtained by heating the nitrate to low redness; it is yellow, fuses at a red heat, and may be obtained as a white hydrate by

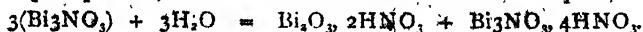
adding ammonia to a solution of one of the bismuth salts; the other oxide (Bi_2O_3) is brown, and furnishes unstable compounds with bases.

A native *sulphide* (Bi_2S_3) is occasionally found crystallised in needles, and is formed as a black precipitate when solutions of the metal are treated with sulphuretted hydrogen.

A *trichloride* (BiCl_3) may be obtained as a very fusible, volatile, and deliquescent substance. It is decomposed by water, and a white oxychloride is formed, while hydrochloric acid is set free.



The *Nitrate* ($\text{Bi}_3\text{NO}_3, 5\text{H}_2\text{O}$) is the most important soluble salt of this metal. It is soluble in excess of acid, but if largely diluted with water a white basic nitrate ($\text{Bi}_2\text{O}_3, 2\text{HNO}_3$) is precipitated, while an acid salt is formed in the liquid—



Bismuth salts generally become milky when their solutions are diluted with water, owing to the formation of an insoluble salt containing excess of the oxide. This precipitate is easily dissolved by acetic acid. Solutions of the alkalis give a precipitate of the white hydrated oxide, not soluble in excess of the alkali. Solutions of the carbonates and phosphates give a white precipitate with bismuth salts; but the yellow, with potassic chromate, insoluble in caustic potash, is used to distinguish bismuth from lead, as the lead chromate is dissolved by excess of potash. Before the blow-pipe bismuth salts on charcoal yield a brittle bead of metal, surrounded by a ring of yellow oxide.

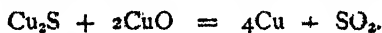
CHAPTER XVI.

I. COPPER. 2. LEAD. 3. THALLIUM.

(60) 1. COPPER: *Symb.* Cu; *Atom. Wt.* 63.5.—This valuable metal is frequently found native, but its most common ore is the sulphide of copper and iron, known as

copper pyrites (Cu_2S , Fe_2S_3); and other less common ores are the green carbonate, *malachite* (CuCO_3 , CuO , H_2O), and the blue carbonate (2CuCO_3 , CuO , H_2O).

In the Welsh process of copper smelting, the pyrites is roasted at a dull red heat, to get rid of portions of the sulphur. The calcined ore is then melted with a siliceous slag, which removes the iron in the form of silicate of the oxide, leaving the copper in the condition of a heavy fusible subsulphide. This is separated from the slag, which floats above it, and is then roasted, so as partly to get rid of the sulphur as sulphurous anhydride, and partly to convert the copper into oxide. When this point is reached, the smelter stirs in this oxide, and mixes it with undecomposed cupreous sulphide. The copper, both from the oxide and the sulphide, then becomes reduced to the metallic state, and the sulphur and oxygen pass off together as sulphurous anhydride—



The crude or *blistered* copper thus obtained is then melted in large quantities in a reverberatory furnace, where it is *poled*; that is to say, the trunk of a young tree is thrust into the melted metal, and thus the last portions of oxide are reduced to the metallic state by the combustible gases given off by the wood, and the copper is brought into the pure and tough condition in which it is required for use.

Copper is a tough, tenacious, and somewhat hard metal, with a well-known red colour. It emits a peculiar odour when rubbed. It may be drawn into very fine wire, can be rolled into foil, and hammered into leaf. It is an excellent conductor of electricity and of heat. When required in a state of perfect purity, it may readily be deposited in sheets from a solution of its sulphate by the current from one or two cells of the voltaic battery. It tarnishes when exposed to the atmosphere; and if heated to redness in the air, a layer of oxide is formed upon the surface, which scales off if be suddenly quenched in water, leaving the metal bright beneath.

Nitric acid dissolves copper with violence, giving off red fumes of nitrous anhydride. Sulphuric acid in the cold does not attack the metal; but if the strong acid be boiled upon it, the copper is dissolved, cupric sulphate is formed, and sulphurous anhydride is set free.

- Copper melts at a bright red heat, or 1090°C . It is extensively used in the manufacture of boilers, kettles, saucepans, and the like; also for the sheathing of ships; and it enters into the formation of many useful alloys, brass being a mixture of about 2 parts of copper and 1 of zinc, and bell metal and bronze, which are alloys of copper and tin. Some of the compounds of copper are used as pigments.

There are two oxides of copper: the red, or cupreous, oxide (Cu_2O), and the black, or cupric, oxide (CuO). It is the latter which furnishes the important salts of the metal. The hydrated red oxide is easily obtained by dissolving 1 part of cupric sulphate and 1 of grape-sugar in water, adding a solution of potash till the precipitate of hydrated cupric oxide is redissolved, and then boiling the solution. A crystalline precipitate of cupreous oxide is deposited. This oxide is used for colouring glass of a ruby red.

Cupreous oxide is soluble in ammonia, and forms a colourless liquid, which turns blue directly that it is exposed to the action of oxygen.

Exp. 248.—To a solution of cupric sulphate add ammonia in excess; introduce the solution into a bottle with some copper turnings. Cork up the bottle securely, and place it in water; heat it for some hours nearly to boiling. The blue solution will gradually become colourless, and a portion of the copper will be dissolved, the cupric becoming converted into cupreous oxide. When cold, pour a little of the colourless liquid upon a white plate: it will absorb oxygen instantly, and will become blue.

Cupric oxide (CuO) may be best obtained pure by dissolving pure copper in nitric acid, evaporating the blue solution to dryness, and decomposing the nitrate by heating

it to redness in a clay crucible for a considerable time. Nitrogen and oxygen are expelled, and cupric oxide is left as a black powder. It is soluble in acids, and furnishes the blue and green salts of the metal. A solution of any one of these salts, such as the sulphate, when decomposed by potash, gives a pale blue hydrated cupric oxide, which, when boiled in water, becomes black and anhydrous. Ammonia gives a similar precipitate, which is redissolved by an excess of the alkali, furnishing an intensely blue liquid, characteristic of copper.

The sulphate, or blue vitriol ($\text{CuSO}_4, 5\text{H}_2\text{O}$), is its most important salt. It is easily obtained on the large scale by boiling metallic copper with oil of vitriol diluted with half its bulk of water. It crystallises in beautiful blue prisms, which, when heated, lose water, and crumble down to a white powder.

Cupric chloride ($\text{CuCl}_2, 2\text{H}_2\text{O}$) may be obtained by dissolving the carbonate or the oxide in hydrochloric acid, and evaporating. Its crystals are green, and form a green solution, which becomes blue on dilution. When heated, it loses water, and then half its chlorine, cupreous chloride (CuCl) being formed. Cupreous chloride is also formed when a solution of cupric chloride in hydrochloric acid is digested on copper in closed vessels; it crystallises gradually in transparent tetrahedra, insoluble in water, but soluble in excess of hydrochloric acid.

Cupreous sulphide (Cu_2S) is occasionally found native, as is also the *cupric sulphide* (CuS), which is precipitated as a brownish-black hydrate when a solution of a cupric salt is exposed to the action of sulphuretted hydrogen.

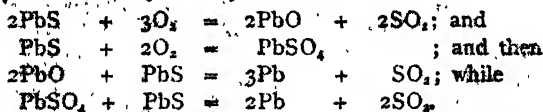
Tests for Copper.—In addition to the characteristic blue liquid formed in solutions of cupric salts by the addition of excess of ammonia, they are known by their forming a brown precipitate with potassic ferrocyanide, and by the deposit of metallic copper which is produced on a polished plate of iron, if plunged into a feebly acid solution of a cupric salt.

Before the blow pipe, on charcoal in the reducing flame, compounds of copper furnish a red malleable bead of the metal.

Copper salts produce vomiting when swallowed, and act as powerful irritant poisons.

(61) 2. LEAD: *Symb.* Pb; *Atom. Wt.* 207.—This useful metal occurs tolerably abundantly in the form of sulphide, or *galena* (PbS), which is its only ore of importance, although it is found both as carbonate and as sulphate, and in one or two other minerals.

In extracting the metal the sulphide is roasted on the hearth of a reverberatory furnace. Sulphur burns off, and a mixture of oxide and sulphate of lead is formed. These substances are at intervals stirred by the workman into the melted mass of sulphide beneath. The oxide and sulphate, as well as the sulphide, give up their lead in the metallic state, and the sulphur and oxygen pass off as sulphurous anhydride. Galena yields by oxidation—



Lead is a soft, bluish-white, brilliant metal, of little tenacity. It melts at a temperature of 327°C ., and may with some difficulty be crystallised by slow cooling. It shrinks as it becomes solid, and hence is not well fitted for castings. If exposed to a damp atmosphere it soon tarnishes, and an adherent layer of oxide forms upon the surface. If heated in a current of air, when melted, the metal oxidises quickly, and furnishes an oxide, which melts at a full red heat. During this operation it emits white fumes, owing to a partial volatilisation at a high temperature. Nitric acid, when somewhat diluted, dissolves the metal rapidly, but sulphuric and hydrochloric acids have but little effect upon it. It is on this account that sulphuric acid is made in chambers lined with lead.

Lead is extensively used in the construction of cisterns, gutters, and pipes for the storage and distribution of water; also for roofing. It enters into many valuable alloys, such as pewter, type-metal, and plumbers' solder; and is used in the form of oxide in making glass. The carbonate, oxychloride, and chromate are largely employed as pigments.

Lead is a dangerous but insidious poison, producing symptoms of colic and partial palsy. It is apt to accumulate in the body when swallowed in minute quantities; and as it is largely used in the storage of water, it is important to study the conditions under which lead is liable to be chemically acted on.

When lead is exposed to a dry air it does not alter, but *pure* water in the presence of air corrodes it rapidly. The lead becomes oxidized on the surface; the water dissolves the oxide slightly, and this solution absorbs carbonic acid: an insoluble hydrated basic carbonate of lead is precipitated, fresh oxide is formed on the metal, is dissolved by the water, fresh carbonic acid is absorbed, a fresh precipitate is formed; and so the process goes on continuously. The presence in the water of small quantities of many soluble salts, such as from 30 to 60 mgms. per litre, materially alter this result. The corrosion is much increased by the presence of chlorides, nitrates, and nitrites; but it is diminished by the sulphates, phosphates, and especially by the carbonates. Lead oxide is scarcely soluble in water which contains these salts. The water supplied in towns generally holds sufficient calcic carbonate dissolved to prevent it from acting to any injurious extent upon the metal. A film of insoluble basic carbonate is formed upon the surface, and thus the lead beneath is protected from further corrosion. Sometimes, as in the pure lake waters of Scotland, the presence of a little vegetable matter acts as a preservative, by combining with the oxide of lead, and forming an insoluble lining to the cisterns and pipes. Slate cisterns, however, are in all cases to be preferred.

Lead forms four oxides: a black suboxide (Pb_2O); a

protoxide, the important base (PbO) from which the salts of the metal are derived; a brown-dioxide (PbO_2), which is insoluble in the acids; and an intermediate oxide (red lead), a compound of one or of two molecules of the protoxide with one of the peroxide (PbO , PbO_2 , or more usually $\cdot 2\text{PbO}$, PbO_2).

The *protoxide*, or *litharge* (PbO), is commonly obtained, by heating the metal in a current of air, as a pale yellow scaly mass. It fuses at a full red heat, and is a valuable flux to the assayer; but it speedily penetrates and destroys the crucibles in which it is melted. A solution of a salt of lead, such as plumbic nitrate, furnishes, on the cautious addition of potash or soda, a white precipitate of the hydrated oxide; it is soluble in excess of the alkali. Lead oxide is a powerful base. It is readily soluble in the acids, and has a strong tendency to form salts which contain an excess of base.

Exp. 249.—Dissolve 2 or 3 grams of lead acetate in 200 or 300 c. c. of water, and boil it with a grain of finely-powdered litharge: the oxide will gradually be dissolved, and the solution will restore the blue colour to reddened litmus.

Exp. 250.—Blow a little air from the lungs through a short quill tube into a little of the solution in a test-tube: the solution will become filled with white silky scales of the hydrated oxycarbonate of lead (PbO , H_2O , PbCO_3).

This solution consequently furnishes one of the best tests for uncombined carbonic anhydride, whether in air or in water.

Red lead, or *minium*, is obtained by heating metallic lead in a current of air below the point at which the litharge fuses. The oxide is ground with water to a fine powder, and the fine particles, after they have settled down from suspension in water, are heated to about 320°C ., in iron trays, in a current of air for several hours. The oxygen is slowly absorbed, and a fine red crystalline powder is obtained. If heated to redness, the absorbed oxygen is driven off, and litharge is left. Red lead is largely used in making flint glass.

Exp. 251.—Pour a little nitric acid, diluted with 3 or 4 times its bulk of water, upon a few decigrams of red lead: the red colour will disappear, and the brown dioxide (PbO_2) will be left undissolved, whilst lead nitrate is formed.

Lead Sulphide (PbS).—Lead has a very powerful attraction for sulphur. Galena, the common ore of the metal, is the sulphide; it has a deep leaden colour, is hard, brittle, and has a high metallic lustre. It fuses at a full red heat, and is oxidized easily, with escape of sulphurous anhydride, in a current of air.

Exp. 252.—Mix 10 grams of powdered galena with 14 of dried sodic carbonate and 1 gram of powdered charcoal. Place 3 or 4 blacksmith's nails, with their heads downwards, in a Cornish clay crucible; then add the mixture. Cover it with a thin layer of fused and powdered borax. Heat the crucible to full redness for 10 minutes; take out the nails. When cool, break the crucible: a button of lead will be found at the bottom, sulphide of iron being formed, while metallic lead separates. This method is commonly used in the dry assay of a sample of galena.

All the salts of lead, both soluble and insoluble, become blackened when placed in water containing sulphuretted hydrogen.

Lead Chloride (PbCl_2) is sparingly soluble; it is precipitated in crystalline needles on adding hydrochloric acid to a solution of a lead salt.

Lead Sulphate (PbSO_4) is a white insoluble powder produced on adding sodic sulphate or other soluble sulphate to a solution of a lead salt.

Lead Iodide (PbI_2) is yellow and insoluble. It is formed by adding potassic iodide to a soluble lead salt. The *Chromate* (PbCrO_4) is also yellow and insoluble.

Lead Nitrate ($\text{Pb(NO}_3)_2$) is prepared by dissolving metallic lead in nitric acid, and evaporating; octahedral white anhydrous crystals are deposited. Several basic nitrates and nitrites may be formed.

Lead Carbonate (PbCO_3), or white lead, is one of the most

important insoluble compounds of the metal. When ground into a paste with a drying oil (linseed oil being generally used), it forms the basis of our common house paints.

Lead forms a very large number of insoluble compounds. The sulphate, iodide, chromate, and sulphide are often used as tests of the metal. If a water contain lead, even in minute quantity, its presence is easily ascertained by taking two similar jars of 25 cm. high, of colourless glass, filling both of them with the water, and adding to one of the jars 3 or 4 c. c. of a solution of sulphuretted hydrogen. A quantity of lead less than one part in two millions is easily perceived, by the brown tinge occasioned, on looking down upon a sheet of white paper, the jar to which the test has not been added serving as a standard of comparison.

Exp. 253.—Dissolve 30 grams of lead acetate in a litre of distilled water in a flask, and hang up in the solution a lump of zinc. If the glass is left undisturbed for three or four days, beautiful crystalline plates of lead, forming what is often called the 'lead tree,' will be deposited upon the zinc. Zinc will have been dissolved, while the lead, which has a smaller attraction for the radical of the acid, is separated.

Before the blowpipe on charcoal the salts of lead yield a soft, white, malleable bead of the metal, surrounded by a yellow ring of oxide.

¶62) 3. THALLIUM: *Symb.* Tl; *Atom. Wt.* 204.—This is a metal which accompanies certain kinds of pyrites in small quantity. It was discovered quite recently by the beautiful green colour which it gives to flame; and this, when viewed by the spectroscope, is found to be concentrated into a single intense green line. It is a heavy metal, resembling lead in appearance, but it quickly tarnishes in the air. Its principal oxide is soluble in water, and has an alkaline reaction on red litmus. The sulphate, nitrate, and carbonate, are white soluble salts. The sulphide is brownish black; the chloride yellowish-white, and sparingly soluble. *

CHAPTER XVII.

THE NOBLE METALS.

1. MERCURY. 2. SILVER. 3. GOLD. 4. PLATINUM. 5. PALLADIUM.
6. RHODIUM. 7. OSMIUM. 8. IRIDIUM. 9. RUTHENIUM.

(63) 1. MERCURY: *Symb.* Hg; *Atom. Wt.* 200; *Sp. Gr.* at 0°, 13.596; *of Vapour*, 6.976; *Melting Pt.* -39°; *Boiling Pt.* 350°; *Atom. and Mol. Vol.* ; * *Rel. Wt.* 100.

This remarkable and interesting metal, often called *quick-silver*, is the only one that is liquid at common temperatures. It is found in but few places, and then usually as sulphide in the red ore known as *cinnabar*, accompanied by small quantities of the metal itself. It is extracted from this ore by simply roasting it in a current of air, and passing the vapours through long earthen pipes. The mercury condenses, and the sulphurous anhydride passes off into the air. Mercury possesses a lustre like that of polished silver. It volatilises slowly at all temperatures above 4° C.; and when heated, it boils at 350°, giving off a heavy transparent vapour, which is 100 times as dense as hydrogen. It freezes at -39°, and forms a white malleable mass, which contracts suddenly as it becomes solid. When pure, it is not tarnished by exposure to the air; but if kept at a temperature of 300° or 400°, it absorbs oxygen slowly, and becomes converted into crystalline scales of the red oxide. The purity of the metal may be judged of by the perfect mobility and sphericity of its globules, which do not wet non-metallic surfaces. If any other metals, such as zinc, lead, or bismuth, be present, the globules assume an irregular elliptical form, and have a tail-like prolongation as they roll about.

Exp. 254.—Dissolve a fragment of lead of about the size of a mustard seed in 40 or 50 grams of clean mercury. Cork it up in a glass bottle which will hold 200 or 300 c. c. and agitate the

* The molecule of the vapour of mercury, like that of zinc, cadmium, and other metallic dyads, contains only 1 atom of the metal.

mercury briskly : a black film will be found over the surface. Withdraw the cork, blow out the air with a pair of bellows, and then renew the shaking. Repeat this three or four times until the black powder ceases to increase. Then pour the mercury into a cone of writing-paper folded like an ordinary filter, but pierced at the point with a pin-hole, and supported in a funnel : the metal will run through, and leave the oxide of lead, mixed with finely divided mercury, adhering to the paper. If a little finely-powdered loaf-sugar be added before agitating the mercury, the process is effected more quickly.

If a large quantity of mercury is to be purified from foreign metals, it is best to place it in a shallow layer on the bottom of a dish, and to cover it with nitric acid diluted with ten or twelve times its bulk of water, leaving it for a few days at ordinary temperatures, frequently stirring the acid and mercury together ; after which it may be washed, and dried with a cloth.

Mercury is attacked immediately by chlorine and by bromine ; more slowly by iodine. It also dissolves most of the metals, except iron and platinum. Gold, silver, and tin amalgams are used in the arts. It also combines readily with lead, bismuth, antimony, zinc, and copper. The amalgamation is immediately effected by cleansing the surface of the metal with a solution of mercury in nitric acid, and then placing the metal in the mercury.

Nitric acid dissolves mercury with great energy and liberation of nitrous fumes. Hydrochloric acid is without action on the metal. Sulphuric acid, when boiled upon it, dissolves mercury, while sulphurous anhydride is given off ; but it has no action upon it in the cold.

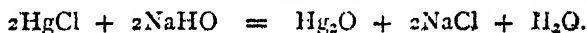
Mercury is used in medicine, mixed, by simple grinding with chalk, into a grey powder ; and when incorporated with a proper proportion of conserve, it forms what is well known as *blue pill*. It acts as a powerful metallic poison. Workmen exposed to its vapours in the operations of gilding suffer from a peculiar tremulous affection, called *mercurial palsy* ; and it often produces salivation, with ulceration of

the mouth and throat. Some of its salts, such as corrosive sublimate, when swallowed, act as immediate and powerful irritants, producing speedy death.

Mercury is largely used in philosophical enquiries. Its expansion in glass is employed as a measure of temperature in the thermometer; and it is not only a requisite in the construction of the barometer, but it furnishes an indispensable liquid in the apparatus used for the accurate collection and measurement of gases.

Mercury forms two oxides: the grey or black oxide (Hg_2O), and the red oxide (HgO): both of them yield salts when treated with acids.

Mercurous Oxide (Hg_2O) is a powerful base, but is unstable when isolated. Exposure to light or to a moderate heat causes it to separate into the metal and the red oxide, Hg_2O becoming $\text{Hg} + \text{HgO}$. It is best obtained by grinding calomel with caustic soda in excess, and washing out the sodic chloride—



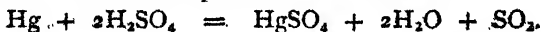
Mercuric Oxide, or the red oxide (HgO), is obtained slowly, in red scales, by heating mercury to 300° or 400° in an open flask with a long neck for some days; but it is more conveniently procured by heating the nitrate cautiously till it is converted into a bright scarlet powder. It may also be precipitated as a yellow powder by adding a solution of potash or soda to one of corrosive sublimate.

The red oxide, when heated, becomes black; and at a higher temperature is separated into metallic mercury and oxygen. It is easily dissolved by acids.

Mercury forms two sulphides, Hg_2S and HgS , the latter, *cinnabar*, constituting the principal ore of the metal. It is formed artificially by subliming mercury with about a sixth of its weight of sulphur, when it furnishes the beautiful red pigment known as *vermilion*. This sulphide is also obtained as a black precipitate by decomposing a soluble mercuric salt with sulphuretted hydrogen in excess.

Mercury also forms two chlorides, calomel (HgCl) and corrosive sublimate (HgCl_2).

Calomel, or *Mercurous Chloride* (HgCl), is a heavy, white, insoluble powder, which may be obtained by mixing a solution of sodic chloride with one of mercurous nitrate; but it is more commonly obtained by converting 4 parts of mercury into sulphate by boiling it to dryness with 6 parts of oil of vitriol, and then grinding the dry mass with 4 parts more of mercury and 3 parts of sodic chloride, and heating the mixture. Mercuric sulphate is first obtained—



This sulphate is then converted, by the additional mercury, into the mercurous sulphate—



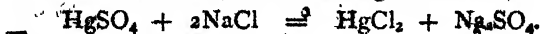
and this, by sublimation with common salt, is converted into calomel and sodic sulphate—



Exp. 255.—Heat a little calomel in a test-tube: it will sublime without melting, and condense on the cold sides of the tube.

Exp. 256.—Place a small quantity of calomel at the bottom of a short quill tube, cover it with a layer of dried sodic carbonate 15 mm. thick, heat the sodic carbonate to redness, and gradually sublime the calomel through it: white metallic globules of the metal will condense in the cold part of the tube.

Corrosive Sublimate, or *Mercuric Chloride* (HgCl_2), is usually prepared by grinding 5 parts of mercuric sulphate with 2 of common salt, and subliming the mixture—



Its fumes are very acrid and poisonous.

Corrosive sublimate melts easily; and when heated further, boils (at 295°), furnishing vapours, which condense in semi-transparent or in white crystals. It is freely soluble in water, alcohol, and ether. It is the most important of the soluble mercuric compounds. It is a strong antiseptic.

Exp. 257.—Whip up the white of an egg with water; strain it

through muslin. Add a little solution of corrosive sublimate : an immediate coagulation of the white of egg will occur. Such coagulated albumen is not liable to putrefy.

Wood, cordage, and canvas are sometimes soaked in a solution of the salt, and are thereby rendered less likely to decay.

Mercuric Iodide (HgI_2).—Add to a dilute solution of potassic iodide a few drops of a solution of corrosive sublimate: a yellow precipitate of mercuric iodide, becoming salmon-coloured, and ultimately brilliant scarlet (HgI_2), is formed. This iodide is redissolved by an excess of potassic iodide, or by one of corrosive sublimate: with the iodide it forms a soluble double salt (KI, HgI_2), and a similar double salt with corrosive sublimate ($\text{HgI}_2, 2\text{HgCl}_2$).

Exp. 258.—Heat a little of the mercuric iodide in a dry test-tube: it will melt and sublime, and condense in yellow crystals. Shake out the sublimate upon a piece of paper, and draw a glass rod firmly across the heap of crystals: a scarlet colour will be produced.

This change is brought about by the conversion of the yellow rhombic plates into a dimorphous red octahedral form by the molecular disturbance occasioned by pressure.

Tests for Mercury.—All the salts of this metal are volatilised by heat. They are all reduced to the metallic state, whether soluble or insoluble, by being boiled with an excess of stannous chloride. If a slip of copper be boiled in a solution of a salt of mercury, it becomes coated with a white amalgam; and if the copper be heated in a small tube to redness, globules of mercury are driven off, and condense upon the sides. *Mercurous* salts give a black precipitate with sulphuretted hydrogen; a white, consisting of calomel, with a soluble chloride; and this white precipitate is blackened by the addition of ammonia, but is not redissolved by it. It is soluble in chlorine water or in boiling nitric acid. *Mercuric* salts give a yellow precipitate with solution of potash, and a white one with ammonia; with sulphuretted

hydrogen a white, passing through brownish-red into black. Their reactions with potassic iodide have been already noticed.

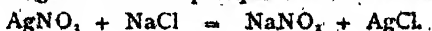
(64) 2. SILVER: *Symb.* Ag; *Atom. Wt.* 108.—This beautiful metal has been known and prized from the earliest ages. It is found commonly in the native state, and almost invariably accompanies galena in small quantity, in the form of sulphide. Mercury is used on a large scale for dissolving metallic silver, and separating it from earthy and other impurities, but the metallurgic processes by which silver is extracted are somewhat elaborate, and are described in the text book on 'Metallurgy.'

Silver has a white colour, with a tinge of red. It possesses considerable tenacity and malleability, so that it may be drawn into very thin wire, and hammered into leaf. It is softer and more fusible than copper, and requires a temperature of 1023° C. for its fusion: though it is scarcely volatile in ordinary furnaces, it may even be made to boil under the very intense heat of the oxyhydrogen jet. As a conductor of heat and electricity, it is unsurpassed. It does not become oxidized at any temperature; but it has a singular power of absorbing oxygen when in a state of fusion, and giving up the gas suddenly when it solidifies. It combines slowly with chlorine, bromine, and iodine. Its attraction for sulphur is very considerable; the brown tarnish that silver acquires by exposure to the air is due to the formation of a thin film of argentic sulphide, in consequence of the action of the metal on the traces of sulphuretted hydrogen occasionally present in the air. This tarnish may be removed by rubbing the surface with a solution of potassic cyanide. Nitric acid is the best solvent for silver; but it may also be dissolved by boiling sulphuric acid, with escape of sulphurous anhydride.

Silver is seldom used alone, as it is too soft to resist wear; but when alloyed with either $7\frac{1}{2}$ or 10 per cent.

of copper, it is extensively employed in coinage and in the manufacture of plate. When a thin layer of silver is applied to the surface of copper or of steel articles, it furnishes what are called 'plated goods.' Mirrors for lighthouses are plated, as from its high lustre silver furnishes the best reflecting surface for such purposes.

Exp. 259.—Dissolve a sixpenny-piece in nitric acid. The solution has a bluish colour, owing to the presence of the copper which is always added before coining, for the purpose of hardening the metal. Dilute the solution with 200 c. c. of water; then add a solution of common salt so long as it forms a precipitate: white flakes of argentic chloride are formed. Stir the mixture briskly with a glass rod: the precipitate will collect into clots—



Filter the solution. The presence of copper may be proved in the clear liquor by adding ammonia in excess to a portion of the liquid: a blue solution is formed.

Exp. 260.—Place the blade of a knife in another portion of the filtrate: it will become coated with metallic copper.

Exp. 261.—Take the precipitated argentic chloride obtained in *Exp. 259*, and after having washed it well on a filter, place it in a test-glass with a little water; add two or three drops of sulphuric acid, and then place a slip of zinc in contact with the chloride, and leave it for twenty-four hours. The chloride will be reduced to metallic silver, which will have a grey porous aspect, while zinc chloride will be found in solution. Lift out the piece of zinc carefully; wash the silver first with water containing a little sulphuric acid, then with pure water. Dry the residue. Place a small quantity of it upon an anvil, and strike it a blow with a hammer: a burnished metallic surface will be produced. Place a little of the grey powder upon charcoal, and heat it in the flame of the blowpipe: it will become melted into a brilliant malleable bead. Dissolve another portion in nitric acid: red fumes of nitrogen peroxide escape, and argentic nitrate is obtained in solution.

Silver belongs to the class of monads; it forms only one oxide of practical importance (Ag_2O). It may be obtained as a brown hydrate by adding caustic potash to a solution

of argentic nitrate. An excess of potash does not redissolve it; but it is easily dissolved by an excess of ammonia. Other oxides (Ag_2O and $2\text{Ag}_2\text{O}_2$) are, however, known.

The most important soluble salt of silver is the *nitrate* (AgNO_3), which crystallises in colourless anhydrous tables; it melts at a moderate heat, and when cast into small round sticks forms the 'lunar caustic' of the surgeon. This salt is readily decomposed by the action of organic matter, especially when exposed to light; hence it is used for the preparation of ink for marking on linen, as the stain cannot be removed by washing with soap. If it fall upon the skin, it blackens it. A strong solution of potassic iodide, or of the poisonous potassic cyanide, will remove these stains from the skin, or from linen.

The *sulphide* (Ag_2S) often occurs naturally, mixed with lead sulphide in small quantity. It may also be precipitated as a black hydrate when any silver salt, soluble or insoluble, is exposed to a solution of sulphuretted hydrogen.

The *chloride* (AgCl) is white, insoluble in water and in nitric acid, even if boiling, but freely soluble in ammonia. If heated to redness, it melts into a horny-looking mass. The precipitated chloride becomes of a dark purple colour when exposed to the light, owing to the formation of a subchloride.

The *bromide* (AgBr) is white, insoluble in water and nitric acid, and sparingly soluble in ammonia.

The *iodide* (AgI) is of a pale yellow, and is nearly insoluble in ammonia.

The chloride, bromide, and iodide of silver may be reduced to the state of metallic silver by fusing them in a clay crucible with half their weight of dry sodic carbonate. For example—



They are all soluble in a solution of sodic hyposulphite, and form an intensely sweet solution with it. When exposed to light in the presence of argentic nitrate and some organic

matter, they undergo chemical changes which form the basis of the common processes of photography.

The formation of the chloride, bromide, and iodide of silver, and the properties above described of these compounds, furnish ready tests for the presence of silver; but the phosphates, chromates, oxalates, tartrates, and citrates all form insoluble precipitates with salts of silver. Copper placed in a solution of silver nitrate or sulphate separates the silver in crystalline plates; zinc also reduces the salt, as does also a stick of phosphorus; but the most beautiful effect is produced by adding a few drops of mercury to a solution of silver nitrate containing 5 or 6 per cent. of the salt. A beautiful crystallisation, known as the 'silver tree,' will be formed in a few days.

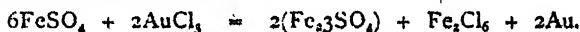
(65) 3. GOLD: *Symb.* Au; *Atom. Wt.* 196.6.—This valuable metal has been known from the earliest times, for it is found in small quantity in almost every country, and it always occurs in the native state alloyed with silver, generally in a proportion varying from 4 to 12 per cent. Many rivers contain it in their sands. In Australia the gold is associated with quartz and slate, and in California it is found in the detritus of quartz and granite. Gold is extracted by a mechanical process of washing, and afterwards dissolving in mercury such portions of the gold as are in a very finely divided state. The mercury is afterwards distilled off, and condensed again for use.

Pure gold is of a rich yellow colour and high lustre; it is nearly as soft as lead. It is very ductile, and is the most malleable of the metals, so that it may be hammered into leaves 11,200 of which would not be thicker than 1 millimetre, or 280,000 would not exceed an inch in thickness. A leaf of gold, attached to a pane of glass, and held up between the eye and a light, will allow a green or purple light to pass through. Gold leaf is extensively used for gilding on wood, papier mâché, and metal, to the surface of which it is attached by means of an adhesive varnish.

Gold fuses at about 1100°C . It is scarcely volatile in the furnace, but in the intense heat of the oxyhydrogen jet it may be dissipated in purple vapours. Sulphuric acid does not attack it; neither does the nitric or the hydrochloric acid separately, but a mixture of the two liberates chlorine, and this gradually dissolves it, forming a yellow solution.

Exp. 262.—Place a little gold leaf in two test-tubes; to one add nitric, to the other hydrochloric acid. Even when heated with the acid the gold leaf remains unaffected. Pour the contents of one tube into the other: the gold will disappear with effervescence. Evaporate this solution in a small porcelain capsule till the acid is nearly all driven off: auric chloride will be left.

Exp. 263.—Dilute the solution with 3 or 4 c. c. of water. To a portion of this liquid add a solution of ferrous sulphate: a brown precipitate of finely divided reduced gold is obtained, and ferric chloride is formed—



This is a common mode of separating gold from its solutions.

Add to another portion of the auric chloride a solution of sulphurous acid: on warming the mixture gold will be precipitated—



A solution of oxalic acid will have a similar effect—



carbonic acid being produced.

All these liquids look purple when viewed by holding them between the eye and the light, owing to the transparency of the finely divided gold.

Gold in its pure state is too soft to be used for the purposes of coin or plate. It is hardened by alloying it with about a tenth or a twelfth of its weight of copper. Gold is usually triad in combination; it however forms two oxides (Au_2O and Au_2O_3), but they are seldom prepared. The *trichloride* (AuCl_3), obtained by dissolving gold in a mixture of nitric and hydrochloric acids, as above directed, is the most important compound of the metal. When heated gradually

to about 175° , it loses chlorine and furnishes aurous chloride (AuCl), a pale yellow, sparingly soluble compound; and by a heat below redness all the chlorine is expelled, and metallic gold is left. A solution of the trichloride is easily decomposed by organic matter. It stains the skin and other organic substances, such as white silk, of a purple colour. Its solution is reduced to the metallic state by many metals, such as copper, mercury, iron, and zinc, as well as by phosphorus, and by several other substances. Stannous chloride, if added to its solution in quantity not sufficient to reduce the whole of the gold, gives a fine purple, known as *purple of Cassius* ($\text{Au}_2\text{Sn}_3\text{O}_6, 4\text{H}_2\text{O}$). It is used for colouring the ruby glass of Bohemia.

(66) 4. PLATINUM: *Symb.* Pt; *Atom. Wt.* 197.—This is a hard, tough, white metal, a good deal resembling silver in appearance, with which in earlier times it appears to have been confounded. It is the densest substance known, except osmium and iridium, which accompany it in its ores, and are equally dense. It may be drawn into very fine wire, and rolled into thin foil. On account of its great infusibility and its power of resisting all acids except a mixture of the nitric and hydrochloric, it is extremely valuable to the chemist, as it furnishes him with crucibles and other apparatus in which he can in most cases where accuracy is required fuse and heat the various bodies subjected to analysis. It is also used as the negative metal in Grove's voltaic battery.

Platinum is of comparatively rare occurrence. It is found in metallic grains, sometimes associated with gold, silver, copper, iron, and lead, but it is almost always accompanied by certain other metals, which are never found without it, viz. palladium, osmium, iridium, rhodium, and ruthenium.

On account of the extreme infusibility of platinum, it requires a peculiar and complicated mode of treatment. The ore is treated first with nitric acid, to dissolve out the common metals; then washed, and treated with hydrochloric acid,

and again washed ; after which the residue is digested at a very high temperature in 4 parts of hydrochloric acid, to which about 1 part of nitric acid is added little by little. When nothing more is dissolved, the acid liquor is decanted, and mixed with a strong solution of sal ammoniac. Most of the platinum is thus precipitated as a yellow double chloride of ammonium and platinum ($2\text{H}_4\text{NCl} \cdot \text{PtCl}_4$). This is washed and then heated ; the whole of the ammonia and chlorine are expelled, and the platinum is left as a grey porous mass, commonly known as spongy platinum. This is then pressed, and forged at a high heat into bars or plates, which are afterwards hammered into dishes or vessels, rolled into sheets, or drawn into wire. This method is now, however, gradually being displaced by a mode of melting the ore by means of the oxyhydrogen blowpipe.

Platinum, if heated alone, does not combine with oxygen at any temperature, but it becomes slowly oxidized if heated with the caustic earths or alkalis. It alloys readily if ignited with lead, tin, bismuth, antimony, or any of the more fusible metals, which would melt a hole in a platinum crucible if heated in it.

Platinum belongs to the group of tetrad metals. It forms two oxides (PtO and PtO_2). They both correspond to salts of the metal, but these are seldom prepared. Platinous oxide (PtO) is soluble in a solution of potash, furnishing a dark olive-green liquid ; and the alkalis also combine and dissolve platinic oxide (PtO_2).

There are two chlorides. *Platinic Chloride* (PtCl_4) is the salt obtained by dissolving platinum in a mixture of hydrochloric and nitric acids, and evaporating the solution to dryness at 100°C . It is an orange-coloured deliquescent substance. If heated for some time to about 235°C . it loses half its chlorine, and becomes converted into the olive-coloured insoluble platinous chloride (PtCl_2). At a heat below redness the whole of the chlorine is driven off, and metallic platinum is left. Platinic chloride forms double salts with the chlorides of the alkali metals ; that with potas-

sium (2KCl , PtCl_4) forms yellow octahedra, insoluble in alcohol, and nearly so in cold water. The ammonium compound ($2\text{H}_4\text{NCl}$, PtCl_4) is commonly employed to separate platinum from its solutions. The sodium salt (2NaCl , PtCl_4 , $6\text{H}_2\text{O}$) is soluble, and crystallises in long red needles. All these salts are decomposed at a red heat : metallic platinum is left, and by washing may be obtained free from the alkaline chlorides.

Solutions of platinic salts are not reduced by ferrous sulphate, but they are so by mercurous nitrate, which precipitates finely divided metallic platinum. Oxalic acid does not reduce them, but a solution of a formiate will, if heated with a neutral solution of platinum, cause the metal to be separated in a powder.

5. *Palladium* is a white metal, nearly as infusible as platinum. It forms a brown solution when dissolved in nitric acid.

6. *Rhodium* is a very hard white metal, very difficult of solution, even in the mixture of nitric and hydrochloric acids. Its salts are of a beautiful rose colour.

7. *Osmium* occurs in extremely hard scales alloyed with iridium and ruthenium. When heated in a current of air, it becomes oxidized, and gives off a remarkable volatile oxide (OsO_4), which has a peculiar pungent smell, and is freely soluble in water. Osmium is the least fusible of the metals.

8. *Iridium* accompanies osmium in the ore of platinum, and is sometimes found native and nearly pure. It is a white, very hard, and brittle metal, which furnishes three oxides. They pass readily one into the other, and furnish salts which differ in tint ; hence the name Iridium, from *iris*, the rainbow.

9. *Ruthenium* is a very hard brittle metal, scarcely fusible before the oxyhydrogen blowpipe. It absorbs oxygen at a red heat, and yields several oxides.

These metals last mentioned are found, in small quantities, accompanying the ore of platinum ; but they are so rare as not to need further description.

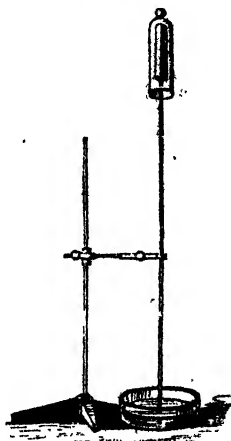
APPENDIX.

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This tendency of gases to mix may be shown in a still more striking manner by the following highly instructive experiment. Adapt to one end of a glass tube, about 1,000 mm.

long and 10 mm. wide, by means of a well-fitting cork, a short circular porous cell, such as is used for galvanic batteries; cover the cork with a layer of sealing-wax. Support the tube in an upright position, with the open end dipping under water, and invert a glass bell jar over the porous cell (fig. 21A). Now pass up hydrogen into the jar: immediately gas will escape from the open end of the tube; the hydrogen passing more rapidly through the sides of the porous cell than the oxygen and nitrogen (air) can pass out, thus forcing these latter out of the tube. So soon as the bubbles cease to escape remove the bell jar: the water now rises in the tube owing to the rapid diffusion of the hydrogen into the atmosphere.

Fig. 21A.



By the aid of this apparatus the student can investigate for himself the phenomena of diffusion; he will find that whenever the porous cell is surrounded by a gas lighter than air, bubbles will escape from the tube; when surrounded by a denser gas the water will rise in the tube, the rise being strictly proportional to the density of the gas.

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Detection of Nitric Acid or Nitrates.

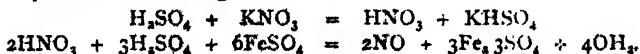
Exp. 93.—Add to a fragment of a nitrate in a test-tube a few scraps of copper and pour on it three or four drops of sulphuric acid. Heat the mixture gently; red fumes will be given off, and may be distinguished

readily, even when very small in amount, by looking through the tube obliquely over a sheet of white paper.

The sulphuric acid decomposes the nitrate, setting nitric acid free; and this in its turn is decomposed by copper with formation of nitric oxide, which unites with the oxygen of the air to form the red fumes of nitrogen peroxide.

Exp. 94.—Dissolve a crystal of a nitrate in a little water in a test-tube; now add carefully an equal volume of concentrated sulphuric acid, cool the mixture perfectly, then pour in a cold solution of ferrous sulphate so as to form a layer above the acid mixture. A characteristic dark brown ring will be formed at the line of contact of the liquids.

In this case the sulphuric acid reacts on the nitrate, producing nitric acid, which is deoxidised by the ferrous sulphate, nitric oxide, ferric sulphate and water being formed—

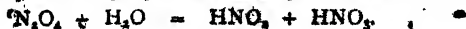


The brown ring is a solution of the nitric oxide in the excess of ferrous sulphate, as the following experiment proves.

Exp. 95.—Introduce concentrated solutions of about five grms. of potassic nitrate and 25 grms. of ferrous sulphate into a flask closed by a cork through which a bent tube and tube funnel are passed (fig. 22). Pour in about eight grms. of sulphuric acid through the funnel and warm gently: a gas is evolved (nitric oxide) which forms red fumes with the oxygen of the atmosphere. Pass the gas into a cold solution of ferrous sulphate: a dark brown solution is obtained. Afterwards pass the gas through a warm solution of ferrous sulphate: the nitric oxide does not dissolve in this case, and, if protected from the air, the solution remains colourless, thus proving the necessity of employing cold solutions when testing for nitric acid.

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Water decomposes nitrogen peroxide, forming nitrous and nitric acids—



Nitric Anhydride (N_2O_5).—Owing to the fact that this body decomposes spontaneously it is extremely difficult to prepare. It has been obtained by decomposing silver nitrate with chlorine—



Nitric anhydride is a white crystalline substance, which is converted by water into nitric acid—



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The formation of potassic chlorate by the action of chlorine on the hot solution of potash is at once explained by the fact that on heating a solution of potassic hypochlorite it splits up into potassic chlorate and potassic chloride—

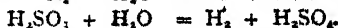


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Anhydrous hydrofluoric acid has been obtained by strongly heating the compound (KF, HF) in platinum vessels, when it breaks up into potassic fluoride and hydrofluoric acid. The latter is condensed in a well-cooled receiver, to a colourless, transparent, mobile liquid, which boils at 19.40° , and does not attack glass, provided all moisture be excluded.

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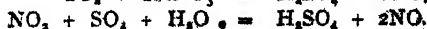
Whereas bleaching by chlorine is generally a process of oxidation, bleaching by sulphurous acid is always a process of reduction : chlorine decomposes water, setting free oxygen ; sulphurous acid in the presence of a body prone to take up hydrogen decomposes water, setting free hydrogen, itself combining with the oxygen—



The bleaching is therefore in both cases usually the result of a secondary reaction.

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The following equations represent the reactions which occur in the process—



The nitric peroxide in contact with water and SO_2 is again reduced to nitric oxide, &c.

QUESTIONS FOR EXAMINATION.

THE following questions have been framed in accordance with the Syllabus issued by the Science and Art Department of the Committee of Council on Education, under the head of 'Inorganic Chemistry. First Stage or Elementary Course—Second Stage or Advanced Course,' pp. 90, 91.

The student will do well to exercise himself from time to time in answering these questions without reference to the text; and the general reader will find his knowledge of Chemistry become much improved by adopting the same course. Should he not be able to answer any particular question, he will have to refer to the page of the book as indicated in the right-hand column, but he is recommended not to write his answer immediately, but to wait until he has thoroughly mastered the text. The answer should as far as possible be given in the student's own language, not in that of the book.

Teachers who prepare their lectures from this book are recommended to set their pupils a number of these questions the day after each lecture: the answers are to be written in full, and marks given to each paper. Those pupils only who thus acquire a certain number of marks should be allowed

to compete for the prize or prizes at the end of the term or half-year.

The Teacher can easily frame other questions on the text, and he is recommended to exercise his class in the use of chemical formulæ and the numerical statements connected therewith, the measurement of gaseous volumes, the conversion of Fahrenheit into Centigrade degrees, the use of the metric system, &c.

C. T.

NO. OF QUEST.		PAGE
1.	Give a definition of Chemistry	2
2.	What is the difference between a simple and a compound body?	2-5
3.	What do you mean by the words analysis and synthesis?	3
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